DREDGED MATERIAL RESEARCH PROGRAM
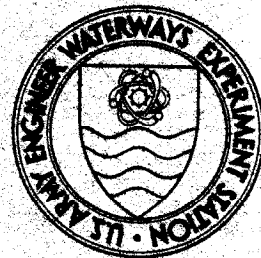
RESEARCH STUDY ON THE EFFECT OF DISPERSION, SETTLING, AND RESEDIMENTATION ON MIGRATION OF CHEMICAL CONSTITUENTS DURING OPEN-WATER DISPOSAL OF DREDGED MATERIALS
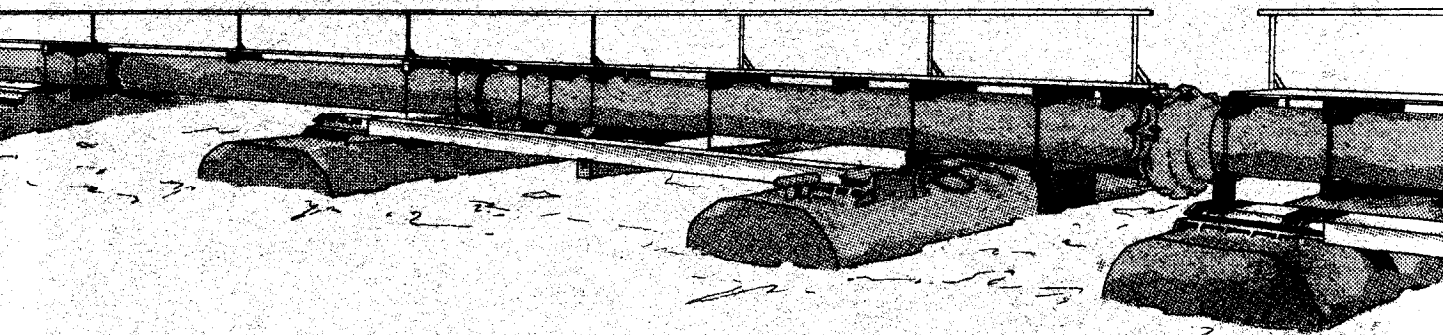
by

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IN REPLY REFER TO: WESYV

28 February 1976

SUBJECT: Transmittal of Contract Report D-76-1

TO: All Report Recipients

1. The contract report transmitted herewith represents the results of one of several research efforts completed as part of Task 1C (Effects of Dredging and Disposal on Water Quality) of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 1C is part of the Environmental Impact and Criteria Development Project of the DMRP. Among other considerations this project includes determining on a regional basis the short- and long-term effects on water quality due to dredging and discharging bottom sediment containing pollutants.

2. This research was conducted as Work Unit 1C06 to study the effect of dispersion, settling, and resedimentation on migration of chemical constituents during dredging and open-water discharge of dredged material. Specific objectives were to evaluate thoroughly sorption-desorption reactions of various contaminants and chemical constituents as affected by physical dilution during aquatic disposal of dredged material, to evaluate the amounts of chemical constituents that may leach from a dredged sediment as it disperses and settles through the water column, and to evaluate the long-term migration of chemical constituents from the resettled sediment. Dredged material from saline and freshwater locations was evaluated.

3. This report includes both qualitative and quantitative evaluation of chemical constituents that usually respond to changes in biological, electrochemical, and physicochemical conditions in sediments: iron, manganese, mercury, copper, lead, chromium, zinc, arsenic, cadmium, nickel, silicate, sulfide, nitrate, nitrite, ammonium, organic nitrogen, and orthophosphate. Chemistry of chlorinated hydrocarbons and organometallic complexes as related to their availability for biological uptake was also studied. The main approach of this study involved the use of laboratory experiments simulating the impact of open-water disposal of dredged sediments on water quality. Special efforts were devoted to quantifying the migration of trace contaminants and nutrients under various conditions as both fresh and marine sediments are resuspended and
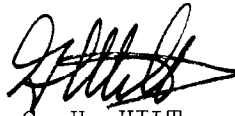
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resettled in water columns. The investigation has shown that concerns
regarding the release of any significant quantity of toxic materials
into solution phase are unfounded. However, the trace metals and chlo-
rinated hydrocarbons associated with macromolecular organics and sus-
pended particles released to the water column may have some unknown
effect.

4. The results of this study are particularly important in evaluating
the water-quality impacts of aquatic disposal of sediments containing a
wide range of constituents, both natural and unnatural. To assess these
effects, regional information on the quality of dredged material, methods
of disposal, and the nature of the aquatic media in which they are dis-
posed is needed. In addition, fundamental information is needed on
contaminant-to-sediment attachment mechanisms. Finally, methods need to
be developed to predict, prior to dredging and disposal operations, the
nature and significance of the effects of the operations on water
quality.

G. H. HILT
Colonel, Corps of Engineers
Director

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Dispersion   Resedimentation
Dredged material disposal   Settling

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

An extensive study on the effect of dispersion, settling, and resedimentation on the migration of chemical constituents during open-water disposal of dredged material shows that concerns regarding the release of any significant quantity of toxic materials into solution phase are unfounded. However, the study indicates that trace metals and chlorinated hydrocarbons associated with macro-molecular organics and suspended particles released to the water column as a result of dredging may have some unknown effect. For example,   (Continued)

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20. ABSTRACT (Continued)

the availability of these organic compounds as a food source for filter-feeders and algae may present some potential problems. Water and sediment samples collected from marine and freshwater environments and subjected to laboratory experiments simulating the impact of open-water disposal on water quality provided data to quantify the migration of trace contaminants and nutrients under various conditions during resuspension and resettling. Also presented are the results of an investigation of the chemistry of chlorinated hydrocarbons and organo-metallic complexes as related to their bioavailability.

PREFACE

This report presents the results of an extensive laboratory investigation on the effect of dispersion, settling, and resedimentation on migration of chemical constituents during open-water disposal of dredged materials under Contract No. DACW39-74-C-0077 dated March 6, 1974, between the U. S. Army Engineer Waterways Experiment Station (WES) and the University of Southern California.

The research described herein was conducted under the supervision of Dr. Kenneth Y. Chen, Associate Professor, Environmental Engineering Program, University of Southern California. Individual team members having primary responsibility for the major technical sections of the study include: S.K. Gupta for geochemical fractionation of sediments, A.Z. Sycip for the column settling study, J.C.S. Lu for long-term sediment-water interfacial phenomena and geochemical fractionation after long-term incubation, M. Knezevic for organo-metallic interactions, and W.W. Choi for associations of chlorinated hydrocarbons. Drs. T.F. Yen and R.A. Lockwood assisted in various phases of discussion, and Ms. L. Koss assisted in report preparation.

The contract was monitored by Mr. J.D. Westhoff, Chief of the Analytical Laboratory Group of the Environmental Effects Laboratory (EEL), WES, under the direct supervision of Dr. Robert Engler, Manager of the Environmental Impact and Criteria Development Project. The Director of WES during the study and preparation of the report was COL G.H. Hilt, CE; Technical Director was Mr. F.R. Brown; Dr. John Harrison was Chief, EEL; and Drs. R.T. Saucier, J.W. Keeley, and F.H. Griffis were the special assistants, EEL, WES. Contracting Officer was Mr. A.J. Breithaupt.

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CONVERSION FACTORS, U.S. CUSTOMARY TO METRIC (S.I.) UNITS OF MEASUREMENT

U.S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

Multiply	By	To Obtain
inches	0.0254	meters
pounds (mass)	0.4535924	kilograms
feet per second	0.3048	meters per second

LIST OF NOTATIONS

Technical Terms

Chemical oxygen demand .... COD

Double distilled (water) .... D.D.

Dissolved oxygen .... D.O.

Immediate oxygen demand .... IOD

Total organic carbon .... TOC

Total organic carbon content of
sediment .... TOC_{sed}

Total organic carbon contents obtained
through successive extractions
with NaOH .... $TOC(NaOH)_{sx}$

Total organic carbon content of humic acid.. TOC_{HA}

Total organic carbon content of fulvic acid..TOC_{FA}

Total dissolved sulfide .... ΣS_D

Total volatile solids .... TVS

EXECUTIVE SUMMARY

In recent years, the Corps of Engineers has dredged an annual average of 380,000,000 cu yd of sediments for the maintenance of the nation's waterways, 65% of which is disposed of in open waters. During the past few years, concern over ecological impacts and the release of toxic substances into water columns has brought this practice almost to a halt. These environmental and water-quality considerations have made it imperative that more knowledge be gained in order to resolve the problem, either by resorting to alternative disposal methods or by mitigation of dredging impact if the resulting environmental impacts are determined to be significant.

Most metal cations and nutrients can exist in several forms which differ in toxicity and availability. Sorptive behavior and redox reactions of various chemical contaminants occurring within sediments during aquatic disposal and after redeposition govern to a large extent the distribution of chemical constituents among various available and non-available forms.

An extensive laboratory study and analytical characterization of the water-quality effects from the soluble constituent fraction resulting from large-scale disposal of contaminated dredged sediments have been carried out. The chemical constituents included in this study are those which usually respond to changes in biological, electrochemical, and physicochemical conditions in sediments: iron, manganese, mercury, copper, lead, chromium, zinc, arsenic, cadmium, nickel, silicate, sulfide, nitrate, nitrite, ammonium, organic nitrogen, and orthophosphate. Chemistry of

chlorinated hydrocarbons and organo-metallic complexes as
related to their availability for biological uptake was
also studied.

The main approach of this study involves the use of
laboratory experiments simulating the impact of the open-
water disposal of dredged sediments on water quality. Spe-
cial efforts were devoted to quantifying the migration of
trace contaminants and nutrients under various conditions
as both fresh and marine sediments are resuspended and
resettled in water columns.

Water and sediment samples for this laboratory study of
marine and freshwater environments were obtained from the
Southern California area. Sediment samples of silty sand,
sandy silt, and silty clay types were characterized with
respect to physicochemical properties including particle-
size distribution. The sediments were also analyzed for
total concentrations of metal species in sediments, non-
residual fraction (including interstitial water, solubility
of solid minerals, ions on exchange sites, metal carbonates,
easily reducible phases, organics and sulfides, iron ox-
ides), lithogenous fractions (mineral residue), and attach-
ment of trace metals and chlorinated hydrocarbons to the
macromolecular organic complexes.

Among the metal species in various geochemical frac-
tions of sediment, the fractions of the interstitial waters
and water soluble phase are considered to be immediately
available for biological uptake upon resuspension of sedi-
ments. However, these fractions represent only an extreme-
ly small part of the potentially available portion--the
non-residual fraction. The magnitude of the non-residual
fraction, which consists of metal species from land source
pollution and marine derivation in contrast to that derived
from the crystalline structure of minerals, ranges from a

low of 1.4% for copper to a high of 98% for cadmium. The non-residual fraction constitutes the reservoir for potential subsequent release of contaminants into water columns and into new interstitial waters. The residual phase is not considered to be available for biological uptake. Therefore, total concentrations of constituents in sediments are not deemed to be the proper criteria for determining the acceptability of dredged sediments for disposal. The availability for biological uptake should be the determining factor for setting up criteria.

In order to evaluate the release of chemical species upon disposal of dredged materials, sediment-water mixtures were resuspended in the water column under different redox and agitation conditions, and observed for a period of 48 hours in order to determine the migration of chemical species. A total of more than 24 sets of experiments were carried out. By integrating the area of each chemical species in a time-concentration scale and dividing it by the length of experimental time, an average value of release is obtained for each species. The concentrations of chemical species in solution compared with those of background concentrations in seawater show that basically no change occurs in concentrations of silver, cadmium, and mercury under all experimental conditions. Concentrations of chromium, copper, and lead were found to be released from 3 to 10 times over the background seawater levels. Iron, manganese, and zinc were released in even larger quantities. The release of trace metals from freshwater sediment in a seawater environment is somewhat larger than the release from marine sediment. Due to the extremely low levels of trace metals in seawater, the relative quantity of release is not considered to be a proper indicator of the effect on water quality. Instead, the level of contaminants released in the water column should be the deciding

factor. Since the concentrations of these metal species in the water column are mostly in the sub-ppb to ppb ranges (with the exception of iron) after the disposal of dredged materials, the short-term release of metal species is not considered to be a serious problem.

Nitrogen and phosphorus compounds are found to be released in the sub-ppm range in the water column, while the concentration of soluble silicate increases to the level of 10 - 20 ppm. The silty clay-type sediment was found to release higher concentrations of nutrients and lower concentrations of trace metals. It is obvious that at such levels of release, autotrophic activity may be greatly increased. This should increase productivity in open waters. No soluble chlorinated hydrocarbons were detected.

After sediments were settled, long-term experiments were conducted to observe the exchange phenomena in the sediment-water interface under rigorously controlled conditions. Water samples in sediment-water interfaces were analyzed for a period of 120 days. The results of long-term observation of sediment-water interfaces show that with the exception of iron and manganese, most of the metals were released in the ppb range under slightly oxidizing conditions, and with little increase or actual decrease under reducing conditions. Iron and manganese were found to be released several hundred times over the seawater background levels under reducing conditions, with iron in the range of 0.1 - 1 ppm, and manganese from 0.01 - 0.1 ppm.

Nitrogenous compounds were released in substantial quantities from clayey-type sediments. Ammonia nitrogen and organic nitrogen can be released to the range of 10 ppm under anaerobic conditions while nitrate and nitrite were increased to the same range under aerobic conditions. Silty and sandy-type sediments were observed to release at a level 2 to 10 times lower than that of clayey sediment.

The concentrations of orthophosphate were in the range of 0.1 to 0.8 ppm under most conditions. Soluble silica increases to 10 - 20 ppm. Chlorinated hydrocarbons were not observed even after three months of experimentation.

The characteristics of the resettled sediments were found to be altered after long-term exposure to different environmental conditions. Under oxidizing conditions, the concentrations of most trace metals in the interstitial water and water soluble phase, as well as easily and moderately reducible fractions, were found to be increased, while those of the sulfide and organic fractions were found to be decreased. Even the concentrations of iron, manganese, nickel, and lead in the mineral residue fraction were found to be converted to other more easily available fractions.

Macromolecular organics such as humic and fulvic substances were extracted and analyzed for association with trace metals and chlorinated hydrocarbons. These macromolecules are believed to be available for filter-feeding organisms and certain species of algae. Even though trace metals associated with the organic fraction are generally below 5% of the total metal contents, this fraction generally contains 2 to 15 times higher concentrations of trace metals than the total sediments on a weight basis.

Concentrations of chlorinated hydrocarbons (chlorinated pesticides and polychlorinated biphenyls) and macromolecular organic compounds were found to be correlated. p,p'DDE generally accounts for 60 - 70% of the total chlorinated hydrocarbon content in sediment, while PCB's (mostly PCB 1254) constitute almost 10 - 20% of the total. Other isomers of DDT and Dieldrin account for the remaining fraction. Concentrations of chlorinated hydrocarbons are also closely related to particles of 8 μm or smaller.

The results show that concerns regarding the release of a significant quantity of toxic materials into solution during dredging operations and disposal are unfounded. The data from this study indicate that while some trace metals may be released in the ppb range, others show essentially no release pattern. Most of the concentrations in soluble phase are well below the allowable concentration levels of the ocean water discharge standards. However, the trace metals and chlorinated hydrocarbons associated with macro-molecular organics and suspended particles released into the water column as a result of dredging activities may present some unknown effect. It is believed that the discrepancy between some field studies which show the release of trace contaminants and this laboratory study which shows very little release may result from the influence of suspended particulates on the concentrations of contaminants.

RESEARCH STUDY ON THE EFFECT OF DISPERSION, SETTLING, AND RESEDIMENTATION ON MIGRATION OF CHEMICAL CONSTITUENTS DURING OPEN-WATER DISPOSAL OF DREDGED MATERIALS

PART I: INTRODUCTION

Need for Corps Research

1. In recent years, the Corps of Engineers has dredged an annual average of 380,000,000 cu yd of sediments, 65% of which is disposed of in the nation's streams, lakes, and coastal waters (1). One of the major areas of concern is the immediate and long-term effect of suspended dredged sediments on water-quality during dredging and disposal operations. Uncertainties about the release of toxic substances and some nutrients from sediments to the water column during disposal have raised many serious questions about the potential water quality impact of such a practice. During the past few years, many worthwhile projects across the country have been unduly delayed for lack of substantive information. Obviously, these unknown effects must be explored so that alternatives or mitigation can be pursued if substantive environmental impact exists.

2. Most metal cations and nutrients can exist in several forms which differ in toxicity and availability. Sorptive behavior and redox reactions of various chemical contaminants occurring within sediments and the water column during aquatic disposal and after redeposition govern to a large extent the distribution of chemical constituents among various available and nonavailable forms. In order to provide basic laboratory data for developing first-

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generation field studies, and to provide an interim guide for Corps of Engineers Environmental Impact Assessments relative to dredging and disposal, an extensive laboratory study and analytical characterization of these effects on water quality has been carried out. The chemical constituents of interest which usually respond to changes in biological, electrochemical, and physicochemical conditions in sediments are: iron, manganese, mercury, copper, lead, chromium, zinc, arsenic, cadmium, nickel, sulfate, sulfide, nitrate, nitrite, ammonium, and orthophosphate. Some of these elements, such as iron and manganese, are major constituents of silicate sediments, while the others usually occur in trace amounts. However, the potential toxicity or availability of some of these chemical constituents make it important to know the conditions under which they may be released into the water column and the amount that may be released.

Dredging Operations in Relation to this Study

3. Sediments are known to contain the major fraction of trace metals, chlorinated hydrocarbons, and nutrients in aquatic environments. The question of whether sediment is a source or a sink for trace metals has been a subject of controversy. Considering the extremely low levels of trace metals found in the present-day ocean, despite the continuous output from land sources, it would seem that sediments are the permanent sink of trace metals. However, changes in dissolved oxygen concentration by currents or by artificial changes through dredging activities, among others, may result in new sediment-seawater equilibria and affect the mobilization of trace metals.

4. During dredging operations, sediment and water are hydraulically intermingled, transported, and disposed

of into the open waters, a dike area, or onto a land site. In the process, migration of chemical species may take place, with the direction of metal transfer being determined by the redox and chemical conditions existing at the time. After dredged material has settled, new sediment-water interfaces are formed. Due to changes in the environmental condition of the overlying water, the chemistry in the interfacial zone will be altered, which will influence the migration of chemical constituents from sediment to water, and vice versa.

5. In general, soluble contaminants are considered to be readily available for biological uptake, while those associated with detrital material can be consumed only by filter-feeding organisms and certain types of algae. Organic matter in the sediment affects to a great extent the behavior of trace contaminants related to their bioavailability. Trace contaminants may interact with organic compounds such as kerogen, humic and fulvic substances, proteins, hydrocarbons, etc., and form complexes with organic colloids which will not only alter the availability but also the toxicity of these substances. The migration of chemical constituents under different experimental conditions is the subject of this study.

Objectives of the Study

6. There are two areas in which information is urgently needed for evaluation of the water-quality impact of open-water disposal: first, prediction of the pollution potential from simple physicochemical tests or characteristics of sediments; and second, the migrations of trace contaminants and nutrients under different environmental conditions. The objectives of this study are to obtain laboratory data for understanding and quantifying those

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phenomena. Specifically:

a. To conduct a thorough laboratory study where sediments subject to dredging are evaluated as to the short and long-term solubilization of constituents from sediments to be dredged. The migration of trace contaminants and nutrients to or from the water column is to be thoroughly characterized by the use of settling column studies. The settling column studies are used to evaluate the amounts of contaminants and nutrients that leach from a disturbed sediment as it disperses and settles through the water column in both fresh-water and marine systems. The capability of a dredged sediment to scavenge or deplete a water column enriched in contaminants or nutrients is also to be completely evaluated. These studies are of particular importance in impounded areas where the effect of water currents would be minimal. The sediments under investigation are thoroughly characterized as to ion exchange capacity, form and location of ions, grain-size distribution, and predominant clay types. This laboratory evaluation is to completely characterize sorption-desorption reactions and kinetics of reactions of various contaminants and chemical constituents of the resuspended dredged material.

b. After a dredged sediment is disposed of in open water, it eventually settles and forms a new sediment-water interfacial zone, where a series of migrations and transformations takes place. Several factors will influence the occurrence of the reactions. Among the more important are the total organic carbon content of the sediment, the

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amount and type of sediment, and concentration and fractionation of chemical constituents. A laboratory evaluation is conducted where simulated sediment-water columns, both freshwater and saline, are created by aquatic disposal of dredged material with a resultant newly-formed sediment-water interfacial zone. A thorough evaluation of the migration of chemical constituents from the sediment of the simulated dredged material disposal site into the soluble portion of the overlying water column is then conducted.

c. Emphasis is placed on use of state-of-the-art technology in closely identifying or measuring the migrations of various chemical constituents. All of the sediment samples used in this study are characterized for the following indigenous properties: pH, percent solids by weight and volume, grain-size distribution, total organic carbon (TOC), total organic nitrogen, nitrate, ammonia nitrogen, total phosphorus, type of sediment, cation exchange capacity, sulfide content, and salinity. This is to obtain data in predicting the water-quality impact from physicochemical characteristics of the sediments.

PART II: REVIEW OF LITERATURE

Introduction

7. Most of the sediments that are dredged from wa-
terways or marine construction sites in coastal water zones
are enriched with contaminants from municipal, industrial,
and surface runoff. The chemistry of contaminated sedi-
ments is of a complex nature, since a great variety of
physical and environmental conditions can affect the chemi-
cal behavior of contaminants and nutrients in the sediments.

8. One of the major areas of concern during dredging
operations is the types of trace contaminants and nutrients
released, and the extent of their release. Upon the
disposal of sediment containing these substances, altera-
tion in water quality ensues at disposal sites under the
different ambient conditions.

9. Dredged material may contain appreciably high
concentrations of pollutants; however, the question arises
as to what quantity of the total concentration of pollu-
tants will be available for immediate release, and what
portion will be released to the water column over a long
period of time. In most instances, analyses of total con-
centrations of chemical species are routinely required in
evaluating the pollutional status of sediments (2); how-
ever, such studies have not yielded information regarding
the partitioning of trace elements among the various frac-
tions of the sediments and their potential to affect water
quality if such sediments are resuspended.

10. Information on the prediction of pollution poten-
tial from physicochemical characteristics of sediments is

lacking. There is not sufficient data to construct a pre-
dictive model to forecast possible alterations in water
quality that can be expected to result from the open-water
disposal of different types of dredged material.

Association of Trace Metals
with Different Sediment Fractions

11. Contaminants and nutrients may exist in various
forms and reside in different fractions of sediment, in-
cluding the soluble form, exchangeable form, existence in
carbonate mineral phase, easily reducible form, interac-
tions with organic and sulfide fractions, association with
a moderately reducible iron oxide or hydroxide, and pres-
ence in the lattice structure of clay and silicate minerals.
Contaminants and nutrients in each fraction may be leached
out under different environmental conditions.

12. The literature (3-13) was reviewed and evaluated
to formulate a sequential chemical extraction of heavy
metals from sediments. The procedure selected for this
study relies heavily on the studies of Presley, et al. (3),
Nissenbaum (4), Chester and Hughes (5), Chao (6), Jackson
(7), and Holmgren (8). It is important to note that none
of the above literature deals inclusively with all the
phases identified previously. From the data presented in
these references, each extractive procedure is considered
to be selective for the corresponding geochemical phase.
However, some interactions are likely. Recently, Engler,
et al. (9), proposed a general scheme for obtaining infor-
mation on the association of trace metals with different
sediment phases. The following extraction procedure is a
further modification of that scheme.

Treatment of Sediment	Geochemical Phase
1. Squeezed through 0.05 μm Millipore filter	Interstitial water
2. Deaerated double-distilled water (Nissenbaum[4])	Water soluble
3. 1.0M ammonium acetate (deaerated)	Exchangeable
4. 1.0M acetic acid (Chester and Hughes[5])	Carbonate, some iron and manganese oxides
5. 0.1M hydroxylamine hydrochloride solution in 0.01M nitric acid (Chao[6])	Easily reducible (manganese oxide and amorphous iron oxide)
6. 30% hydrogen peroxide at 85°C (Jackson[7])	Organic, sulfide
(a) Extract with 1.0M ammonium acetate in 6% nitric acid (pH ~ 2.2)	
(b) Extract with 0.01M nitric acid	
7. (a) Sodium dithionite-citrate (Holmgren[8])	Moderately reducible (iron oxides)
(b) 0.04M hydroxylamine hydrochloride in 25% acetic acid at 100°C for 3 hours (Chester and Hughes[5])	
8. Digestion with nitric acid, hydrofluoric acid, and perchloric acid	Lithogenous fraction

In these schemes, oxidation by hydrogen peroxide and extraction of the trace metals in moderately reducible phase can be carried out using two separate procedures on the same sediment fraction. This can be used to evaluate the merit of each scheme.

13. The successive selective chemical extractions initially leach trace metals originating from land sources pollution and marine-derived fractions (authigenic); final-

ly, the residual fraction of the metals (lithogenic) is dissolved by acid digestion. The part of the sediment which is of the non-residual fraction consists of trace metals associated with the organic matter, sulfides, micro-nodules, and amorphous iron oxides, and those adsorbed on the surfaces of solids. The part of the sediment which is of lithogenous origin (lattice held) consists of trace metals associated with quartz and the fraction of trace metals incorporated in the clay minerals but excluding adsorbed species. Trace metals associated with this part of the sediment will not be available for biological uptake.

14. The non-residual fraction of trace elements will be leached out in the extraction procedure, starting with the water extraction and proceeding by steps through 0.04M hydroxylamine hydrochloride in 25% acetic acid extraction. The trace elements in the lithogenous content will be dissolved only in the mineral acid digestion of the residue after the leaching sequence. The non-residual fraction of metals is further classified into three subgroups:

a. Biogenic fraction: the trace metals associated with organic material and sulfides. This fraction will be leached in a hydrogen peroxide extraction.

b. Nodular hydrogenous fraction: the trace metals residing in the ferro-manganese nodules. This fraction will be leached in an extraction of the easily and moderately reducible phases.

c. Non-nodular hydrogenous fraction: trace metals whose ions are soluble or reside in ion exchangeable phases, together with those associated with carbonates and some amorphous oxides. These fractions will be leached by the sequence of extractions with water, ammonium salts, and acetic acid.

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Migration of Trace Contaminants in
Sediment-Seawater Interface

15.   The transport of trace metals from sediment to seawater may be a result of desorption, chemical reaction, or biological effects. Under reducing conditions, manganese may diffuse to the overlying seawater from sediment (14). In conducting leaching tests, Johnson, et al. (15), found that about one-third of ^{54}Mn was released to the seawater. Data collected by Li and co-workers (16) also show that after burial, manganese may be remobilized under local reducing conditions. Other studies (17-19) show enrichment of manganese and other trace metals such as cadmium, cobalt, copper, iron, nickel, and zinc in the interstitial waters. Lee and Plumb (20) reviewed the literature to predict the release of trace contaminants and nutrients, and concluded that most trace metals could potentially be mobilized with the disturbance of sediment. Wakeman (21) found that chromium, nickel, lead, and zinc were released significantly during the period of a dredging and disposal operation.

16.   The release of trace metals may be due primarily to desorption from iron, manganese, or clay minerals, and also from complex formation. Chloride, bicarbonate, and organo-complexes are probably the predominant species available as complexing agents. Sillen (22) discussed the possibility of the complex formation of trace metals with chloride, hydroxyl, and other ligands in seawater. Feick, et al. (23), found that chloride may cause the release of mercury to the aqueous phase. Formation of organo-metallic complexes may also cause the release of trace metals (24-27). Even though some qualitative information can be obtained from these sources, very little data have been ob-

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tained under well-defined environmental conditions.

Exchange of Nutrients in
Sediment-Water Interface

17. The release of nutrients can be derived from the biodegradation of organic matter deposited on the sediment. Waksman and Hotchkiss (28) showed that the organic matter of the marine sediment can undergo slow but gradual oxidation due to biological activities. Mortimer (29,30) suggested that the oxidation-reduction condition might affect the release rate of nutrients from lake mud. Rittenberg, et al. (31), found that ammonia can be regenerated from sediments and oxidized to nitrate if the Eh value in the overlying water is positive. On the other hand, phosphate can be regenerated under anaerobic conditions. Kemp and Mudrochova (32) found that a minimum of 20% organic nitrogen can be regenerated and released to the overlying lake water from the top 6 cm of sediments. Austin and Lee (33) found that the concentration of NH_3-N increased under anaerobic conditions. Kjeldahl nitrogen was found to increase under anaerobic conditions. NO_3^- was found to be increased to a much higher level in the aerobic system.

18. In studying the release of radioactive phosphorus, Zicker and Berger (34) found that the amount of phosphorus released to the water was very small, with virtually no release from depth greater than 1/4 in. below the mud surface. MacPherson, et al. (35), reported that the release of inorganic-P is pH-dependent. It was found that between pH 5.5 and 6.5, phosphorus can be released at the level of 0.2 ppm. In more acid or alkaline solutions, soluble phosphate is found to increase to the level of 0.3 to 0.5 ppm. These values are quite close to the experimental results of Pomeroy, et al. (36), in that the exchange in the sedi-

ment-water interface tends to maintain a concentration of one μ mole phosphate/liter in the solution phase. McKee, et al. (37), show that the amount of phosphorus transported is proportional to the exposed surface area rather than to the quantity of the sediment. Li, et al. (38), further indicated that the release of inorganic-P into solution under anaerobic conditions is mainly due to the reduction of iron from the ferric to the ferrous state.

19.   Similar to nitrogen or phosphorus, the silicon species also may be released under appropriate conditions. Fanning and Schink (39) report that sediments from the Atlantic sea floor release soluble silicate in large quantities when they are placed in contact with silica-poor seawater, but fail to reduce the concentration of enriched (211 μM) seawater. Elgawhary and Lindsay (40) concluded that there is a tendency for silicate to reach equilibrium value in the long run.

Organo-Metallic Interactions

20.   Many organic substances found in fresh and ocean waters are known to form complexes with metal ions in solution (41-44). Due to the analytical difficulties in determining the speciations, very little, if any, quantitative information is available on the organo-metallic complexes in seawater and marine sediments.

21.   Availability of trace metals to biota in the interfaces between seawater and solid sediment is affected by the organo-metallic interactions. The organic substances and seawater may solubilize the insoluble forms of trace metals attached to the solid surfaces through chelating. Organic ligands from biological debris and synthetic organic materials containing functional groups such as carboxyl, carbonyl, amino, amide, and mercaptans can bind

strongly to the metal ions through coordinate and covalent linkages. Upon incorporation into the sediment, these organo-metallic complexes may undergo further changes. Baturin, et al. (45), proposed that alteration of organic matter in anaerobic sediment is the single most important factor in determining the mobility and availability of heavy metals in sediment.

22. The importance of organic matter in determining the fate of metal species in the sedimentary environment has been repeatedly stressed in the geochemical literature. Saxby (46) summarized the state of affairs rather accurately that there are few well-established facts and many unanswered questions. It has been known for a long time that humic acids play a very important role in the geochemistry of metals in soils, peats, and coals (47-50). Nissenbaum and Kaplan (51) showed that humic compounds are a major component of the organic matter reservoir in recent marine sediments. On the average, humic compounds of the humic acid and fulvic acid type comprise up to 70% of the organic matter. Marine humates were shown by Nissenbaum (52) to be formed in the marine environment and not as detritus, which is generally contributed via run-off from neighboring land masses. Humic compounds are thus assumed to play a very important role in the organo-metallic interaction of sediments.

23. Although the chemical nature of marine humic acids is not clearly known, Nissenbaum (52) suggested their origin by a Maillard-type condensation among amino acids, carbohydrates, and possibly some phenolic compounds.

24. The dynamic nature of humates is expected to play an important role in the diagenesis of sediments. The ability of humates to mobilize trace metals in soils has been known for some time (53-55). By analogy, the same

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may hold true for marine sediments. The information available on marine humates is too meager for any comprehensive answer to the problems of the organo-metal chemistry of sediments. The relative importance of humic compounds as metal carriers in sediments in comparison with other organo-metallic compounds in recent sediments needs to be assessed.

25. Nickel and vanadium porphyrins are frequently cited as important carriers of these metals in sediments (46, 48). The association of organic matter with transition metals may partially explain the often-found large enrichments of trace metals in reducing pore waters over values calculated from metal sulfide equilibria. Presley, et al. (19), reported concentrations of metals several orders of magnitude larger than the concentrations that were calculated from their solubility products in sulfide-containing seawater. This is also confirmed in this study.

26. Little is known at the present time about the chemical bonds which bind the metals to the organic matrix. Some metals may be associated with carbohydrate or amino acid moieties. However, it is possible that the humic acid behaves as a macrocyclic compound towards the metals. Macrocyclic compounds have unusual ion binding abilities (56). Of particular interest is the ability of these compounds to form stable compounds with alkali and alkaline earth metal ions. From a colloid chemistry point of view, these metal ions may be included in the central hydrophilic "cavities" of such molecules, and would then prevent their leaching by an acid or base treatment. Part of the trace metals may be associated with the humic acids by the same mechanism which allows complexation of metal ions by natural polyelectrolytes, such as polygalacturonic or other acids. The addition of such polymers forms insoluble

"sandwich" complexes (57), cages, or micelles.

27. Humic substances are described as linear colloids because they are the size of colloids in at least one dimension, with a molecular weight ranging from 500 to 50,000 gms/mole (58). Only the higher molecular weight fractions exhibit colloidal properties.

Interactions of Macromolecular Organic Compounds with Chlorinated Hydrocarbons

28. A considerable amount of work has been done on the adsorption of chlorinated pesticides on humic substances, clays, or organoclay complexes. Ballard (59) reported that humic substances can act as carriers of DDT in the organic layer of a forest soil. Wershaw, et al. (60), in studying the interaction of pesticides with natural organic materials, concluded that sodium humate can solubilize an otherwise insoluble insecticide, DDT, while humic acid strongly adsorbs 2,4,5-T from solution. It is also suggested that the natural organic polyelectrolytes (humic substances) will interact similarly with other chlorinated hydrocarbons of similar structure. Recently, Pierce, et al. (61), reported that suspended humic particulates may be important agents for transporting chlorinated hydrocarbons through the water column and for concentrating them in sediments and in detritus-feeding organisms.

29. In studying the adsorption of herbicides, Khan (62,63) suggested that the mobility and persistence of 2,4-D in soils and waters will partly be a function of adsorption of the herbicides onto surfaces such as the fulvic acid-clay complex. Interactions of clay with organic matters may facilitate the adsorption of diquat and paraquat on clay minerals in soil. Fredeen, et al. (64),

found most of the DDT to be associated with suspended
solids consisting mainly of clay and fine silts. McDer-
mott, et al. (65), indicated that sediments constitute by
far the largest known benthic reservoir of chlorinated
hydrocarbons along the Southern California coast.

PART III: EXPERIMENTAL

Collection of Sediment and Water Samples

30. Sediment samples from Los Angeles Harbor were collected by box core and grab sampler from the Velero IV and Golden West, ocean-going research vessels operated by the Hancock Foundation of the University of Southern California. The location of the sampling stations is shown in Figure 1. Efforts were made to eliminate all possible contamination during the sampling process. Upon extrusion from cores, these sediment samples were sealed in plastic bags and stored in ice at 4°C for transport to the laboratory, where the well-mixed subsamples were transferred into an airtight plastic container in a glove bag under nitrogen atmosphere. The samples were stored in a refrigeration unit at approximately 4°C until used. At no time were the sediment samples frozen.

31. Seawater from the reference station (three miles outside the breakwater of the harbor, 33° 41.5' N, 118° 14.5' W) was collected during the regular weekly cruise. Each five-gallon polyethylene container was thoroughly cleaned with acid and rinsed with demineralized redistilled water. Water samples were usually used within 24 hours of collection time.

32. Freshwater samples were obtained from Echo Park Lake, operated by the Los Angeles City Recreation and Parks Department. Freshwater sediments were removed from the stream inlet of Morris Dam, located in Azusa, California, with the kind assistance of the personnel of the U.S. Navy Underground Testing Station.

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Apparatus and Reagents

33.　In order to eliminate contamination of the sea-water sample by extraneous trace metals, or the loss of trace metals from the seawater sample, highly sophisticated and elaborate laboratory equipment, meticulous cleaning procedures, and high purity of reagents were required (66-70).

34.　In this experiment, no glassware was used for trace metal study. All containers were made of quartz, Teflon, polypropylene, polyethylene, or tygon material. To eliminate contamination from distilled water, a demineralization and double-distillation unit was installed to produce water suitable for this study. The distilled water was regularly extracted for analysis of trace metals to insure the absence of contaminants. All reagents used were of the highest quality available; for example, ultrapurified acid and double-distilled methyl isobutyl ketone. All labware was soaked in 5% acid for two days and multiply-rinsed with high quality double-distilled water before use.

Selective Extraction of Sediment

Gross concentrations

35.　Trace metals except mercury--The moisture content of 1 g of wet sediment was determined. The sediment was then weighed into a Teflon beaker. The sample was successively digested with 6 ml of nitric acid, 4 ml of hydrofluoric acid, and 3 ml of perchloric acid in a covered Teflon beaker at approximately 175°C. After evaporation to about 2 ml, the sample was diluted to a fixed volume and centrifuged, if necessary, to eliminate solids.

36.　Mercury--About 5 g of well-mixed sample was weighed into an Erlenmeyer flask, and treated with 20 ml concentrated HNO_3 and 15 ml of 2% $KMnO_4$. The flask was

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sealed and heated in a constant-temperature water bath at 70°C for 12 hours. The flask was allowed to cool and the digested sample was then centrifuged. The supernatant was collected in a 100-ml volummetric flask and distilled water added to the mark.

Interstitial water

37.   A portion of homogenized sediment was transferred from the sealed polyethylene bag into the pore water squeezer to collect pore water inside a 2-oz plastic syringe. To avoid contact with atmospheric oxygen, this pore water was immediately filtered through a pre-rinsed 0.05 μm membrane filter under pressure and acidified to around pH 2 with ultrapurified nitric acid.

Water soluble phase

38.   A well-mixed subsample of sediment was transferred into a tared 250-ml polycarbonate centrifuge bottle under a nitrogen atmosphere inside a glove bag. Oxygen-free double-distilled water was added to the bottle to obtain a sediment:water ratio of 1:5. At the same time, another subsample was taken to determine the moisture content and percentage of solids. The centrifuge bottles were sealed and then shaken for 90 minutes. The soluble phase was separated by centrifugation and vacuum filtration through 0.05 μm membrane filter in a glove bag under nitrogen atmosphere. The filtrate was immediately acidified with nitric acid for subsequent analysis of trace metals. To determine the quantity of trace metals dissolved by the added water, the values were corrected for interstitial water concentrations since pore water was included in the sample.

Exchangeable phase

39.   1.0N ammonium acetate (deaerated) solution was

added to the entire residue from the previous step to obtain a 1:6 sediment to extract ratio based on the original sample weight. This step was carried out in a glove bag under a nitrogen atmosphere. Sealed centrifuge bottles were shaken for 90 minutes on a mechanical shaker. The exchangeable phase was separated by centrifugation and oxygen-free vacuum filtration through 0.05 µm membrane filter, as before. The solution was acidified to pH 1 - 2 for trace metal analysis.

Acetic acid extractable phase

40. The residue from the ammonium acetate step was washed with nitrogen-sparged distilled water and centrifuged. The supernatant was discarded. A well-mixed subsample from the residue was transferred into another clean, tared 250-ml plastic centrifuge bottle. The sediment was extracted with 1.0M acetic acid for 90 minutes on a mechanical shaker, according to Chester and Hughes(5). Moisture content and percentage of solids were also determined by taking another subsample. The weight ratio of dry sediment to liquid extractant was approximately 1:50. The extract was separated by centrifugation and pressurized filtration through 0.05 µm membrane filter.

Easily reducible phase

41. The residue from the extraction of the carbonate phase was washed with deaerated distilled water. The washed residue was extracted with 0.1M hydroxylamine hydrochloride in 0.01M nitric acid solution, according to Chao (6), to obtain the trace metals associated with hydrous manganese oxides. The solids to extractant ratio was kept at about 1:50. The mixture was shaken for 45 minutes on a mechanical shaker. The extract was separated by centrifugation and filtration.

Organic and sulfide phases

42. The residue from the previous step was washed with distilled water. Two subsamples from the residue were taken and 3 ml of 0.02M nitric acid were added to each, followed by the addition of 5 ml of 30% hydrogen peroxide acidified to an approximate pH of 2. The mixtures were heated to $85^{\circ}C$ in a water bath for 5 hrs. After 2 hrs of initial heating, another 2 - 3 ml of 30% acidified hydrogen peroxide was added. The mixtures were allowed to cool to room temperature. The first subsample was extracted with 1.0M ammonium acetate in 6% nitric acid, whereas the second subsample was extracted with a 0.01M nitric acid solution (7). The solids were separated as previously described.

Moderately reducible phase

43. Both residues from the previous step were washed with distilled water, which was discarded. The first residue was extracted with a solution of 100 ml distilled water, 8 gm of sodium citrate, and 2 gm of sodium dithionite. The mixture was shaken for 14 hrs on a mechanical shaker, according to Holmgren (8). The extract was separated by centrifugation and filtration through 0.05 μm membrane filter. In this solution, 300 μl of Ultrex nitric acid was added. No precipitation of sulfur was observed. The second residue was treated with 0.04M hydroxylamine hydrochloride in a 25% acetic acid solution. The mixture was heated at $100^{\circ}C$ for 3 hrs. It was then cooled to room temperature, and the extract was separated as described earlier.

Residual (lithogenous fraction) phase

44. A washed subsample from the previous step was

digested successively with 6 ml of nitric acid, 4 ml of
hydrofluoric acid, and 3 ml of perchloric acid, in a
covered Teflon beaker at approximately 175°C. After evap-
oration to approximately 2 ml, the samples were diluted
to a fixed volume and centrifuged, if necessary, to elim-
inate solids.

45. All of the extracts were kept in thoroughly
cleaned plastic bottles. The nitric and acetic acids
used were of Ultrex quality, and the other chemicals were
of analytical reagent grade.

46. The approximate weights of dry equivalent sedi-
ment and volumes of chemical extractants used for selec-
tive extractions are listed in Table 1.

Table 1

Sediment to Extract Ratio

Equivalent Sediment Dry Wt.		Chemical Extractant
1.	22-30 g	125-150 ml nitrogen-sparged double-distilled water
2.	22-30 g	125-150 ml of 1.0M deaerated ammonium acetate
3.	4-5 g	200 ml of 1.0M acetic acid
4.	4-5 g	200 ml of 0.1M hydroxylamine hydro-chloride in 0.01M nitric acid
5(a).	1-2 g	7 ml of hydrogen peroxide and 25 ml of 1.0M ammonium acetate in 6% nitric acid
(b).	1-2 g	7 ml hydrogen peroxide and 25 ml of 0.01M HNO_3
6(a).	1-2 g	2 g sodium dithionite, 8 g sodium citrate,100 ml double distilled water
(b).	1-2 g	40 ml 0.04M hydroxylamine hydrochlor-ide in 25% acetic acid
7.	0.5-0.8 g	6 ml nitric acid, 4 ml hydrofluoric acid, 3 ml perchloric acid

Experimental Setup and Procedure

Column studies

47.   The two columns used in the experiments were
specially designed in two sections: an upper section fabri-
cated from a 5-ft length of 9-1/2-in I.D. plexiglass cylin-
der, 1/4-in thick; and a lower section, a regular commer-
cial 5-gallon plastic pail provided with a hermetically
sealed lid so that the sediment and seawater contained in
it could be saved for continued long-term studies. A
plastic collar bolts onto the column flange to connect the
two sections. Although several sampling ports were provid-
ed along the column, samples were taken mainly at the
middle point, because of the excessive amount of work re-
quired in using the other sampling ports. Gas bubbling
units were located near the base of the column. A sketch
of the column is shown in Figure 2.

48.   Basically, the column test consisted of the dis-
persion of the sediment in seawater at a ratio of 1:20.
Using a glove bag purged with nitrogen gas, 4 liters of
sediment were measured and thoroughly mixed with 16 liters
of seawater. The well-stirred mixture was then poured into
the column holding the remainder of the seawater to make a
total volume of 84 liters. There was less than 30 minutes
elapsed time before the 1:4 slurry was added to the sea-
water.

49.   To simulate dredging conditions as closely as
possible, the column studies were performed under various
conditions. Some of the parameters varied during the test
were:

        a.   type of sediment

        b.   type of water

        c.   dissolved oxygen content of water

<u>d</u>.   degree of agitation

To minimize contamination, all columns, equipment, and
bottles used for storing samples were first thoroughly
washed and then soaked overnight in 5% HCl, and finally
rinsed with deionized distilled water.

50.   Samples were withdrawn from the mid-column with
50-ml plastic syringes and filtered through 0.2 μm Milli-
pore membrane filter. Each time, 250 ml of filtrate was
collected in a precleaned plastic bottle and 200 μl ultra-
purified HNO_3 was added to prevent precipitation and ad-
sorption on the container wall. Samples were taken at
0, 1/2, 1, 2, 4, 8, 12, 24, and 48-hour intervals.

51.   Twenty-four column tests were performed. The
original plan was to obtain a mixture of different types of
experimental settings to simulate a wide variety of field
conditions. Combinations of conditions are shown in Table
2. After preliminary testing, it was found that for the
type of sediments normally encountered in dredging opera-
tions, i.e. anaerobic, there is no substantial difference
between conditions A and C. Therefore, only three experi-
ments were performed for condition C. The last column of
Table 2 shows the corresponding table number for the ex-
perimental data generated under each condition. All column
tests were done using a wet sediment:total seawater ratio
(by volume) of approximately 1:20.

52.   Untreated seawater was used in several tests. To
vary the dissolved oxgen content, nitrogen was prebubbled
into the seawater to simulate a slightly oxidizing condi-
tion, while the compressed air or oxygen was prebubbled
into the seawater for aerobic conditions. All column tests
were performed under room conditions.

53.   Column tests made with agitation were not tested

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as much as those under quiescent conditions because of the difficult filtration of the sediment-laden seawater. In the early stages, no practical way to handle the situation was available. For every 50 ml of filtrate, 8 to 10 pieces of 0.2 µm Millipore filter were required, against a normal 1/3 to 1-piece usage. In later column tests employing agitation by bubbling, the samples were transferred to an Erlenmeyer flask 30 minutes prior to the scheduled time and permitted to settle under a nitrogen atmosphere. The supernatant was then withdrawn with syringes.

Table 2

Column Tests

Group	Seawater/Freshwater Pretreatment	Form of Agitation	Data shown in Tables No.
A	none	quiescent	14-21
B	nitrogen, prebubbled	quiescent	22-27
C	air or oxygen, prebubbled	quiescent	28-30
D	nitrogen, bubbling continued	nitrogen bubbling	31-34
E	compressed air, bubbling continued	compressed air bubbling	35-37

Long-term studies

54. Two different types of long-term experimental tests were set up in a dark temperature chamber ($10 - 14^{\circ}$C): first, disturbed sediment without resettling; and second, disturbed sediment with resettling in a water column.

55. Disturbed, non-resettled test with redox control-- Before contacting with sediment, the seawater was passed through 0.05 µm membrane filter and bubbled with different ultrapurified gases (air, nitrogen, and hydrogen sulfide) to render the seawater in oxidizing, slightly oxidizing, or reducing conditions. After contacting, the ultrapuri-

fied gases were still connected with the experimental system (Figure 3) under the appropriate partial pressure. Dissolved oxygen (D.O.) and total dissolved sulfide (ΣS_D) were checked every two days and at the sampling time to maintain the systems in the desired condition:

    <u>a</u>.   Oxidizing condition: D.O. = 5-8 mg/l; ΣS_D = 0 mg/l

    <u>b</u>.   Slightly oxidizing condition: D.O. = 0-1 mg/l; $\Sigma S_D \leq 0.05$ mg/l

    <u>c</u>.   Reducing condition: D.O. = 0 mg/l; ΣS_D = 15-30 mg/l

56.   The pH values were found to stabilize gradually to an equilibrium condition under different redox conditions. For oxidizing and slightly oxidizing conditions, pH decreased from approximately 8.3 to the range of 7 to 7.5 after about 15 days of contact time. Under reducing conditions, pH remained about 7 during the experimental period.

57.   <u>Disturbed, resettled test without redox control</u>--The sediments were mixed with unfiltered seawater at a 1:4 volume ratio in a glove bag and shaken vigorously for about 10 minutes, then dumped into a 6-ft tall plexiglass cylinder containing 60 liters of original seawater. After two days of resettling, the lowest part of the column was removed with its contents--the sediment and seawater at an approximate ratio of 1:4. This reactor was sealed and placed in a constant temperature-constant humidity room at $10 - 14^{\circ}C$ for a long-term experiment as a closed system.

58.   After resettling, the interfacial water associated with silty clay sediment was in:

    <u>a</u>.   oxidizing condition from 0 to 1/4 day: D.O. > 0.5 mg/l; ΣS_D = 0

    <u>b</u>.   slightly oxidizing condition from 1/4 to 3 days: 0 < D.O. $\leq$ 0.5 mg/l; ΣS_D < 0.05 mg/l

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<u>c</u>.   reducing condition after 3 days:
      D.O. = 0 mg/l; $\Sigma S_D > 0.05$ mg/l

No external control was attempted.

59.   The interfacial water associated with the silty
sand sediment was in an oxidizing condition from 0 to 3
days. After 3 days this became a slightly oxidizing con-
dition and remained in that condition thereafter. For
sandy silt, the condition again changed to an oxidizing
environment after about 45 days, due to leakage in the
reactor lid.

Elemental Partitioning of Sediments after Long-Term Exposure to Different Redox Conditions

60.   The changes of geochemical phases in sediments were
studied after long-term exposure of sediment to different
seawater interfacial conditions after the following periods:
      <u>a</u>.   silty clay sediment--150 days
      <u>b</u>.   silty sand sediment--150 days
      <u>c</u>.   sandy silt sediment--120 days

For the reducing sediments, the reactors were carefully
opened under nitrogen atmosphere. The interfacial water
was drained by syringe without disturbing the sediment.
The surface sediment (about 1 cm from the top) was sliced
by Teflon spatula and immediately sealed in polyethylene
containers for the analysis of geochemical phases. Another
portion of the surface sediment (about 2 cm depth) was
sealed in four 250-ml polycarbonate centrifuge bottles for
interstitial water analysis.

61.   All interfacial water samples were taken from
1 inch above the surface of the sediment. In order to
keep air from contaminating the sample, a syringe pressur-

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ized filtration technique and glove bag setup were used. Samples for trace metals analysis were passed through 0.05 μm membrane filter. In the column study tests, 0.2 μm membrane filters were used due to high loading of suspended solids. For nutrient analysis, 0.45 μm membrane filter was used. For chlorinated hydrocarbons, glass filter paper was used.

62.   Polyethylene bottles were used to store samples for trace metal and nutrient analysis, while pyrex glass bottles were used to store samples for the analysis of chlorinated hydrocarbons. Since the trace metals were at very low levels, special care was necessary in order to eliminate contamination. All containers for trace metals analysis were made of quartz, Teflon, polypropylene, or polyethylene materials and were cleaned by soaking in 5% acid for at least two days and multiple rinsing with high quality demineralized, distilled water.

63.   The 0.05 μm membrane filter was found to be more satisfactory for the separation of soluble from particulate matters. About 20 ml of filtrate was discarded before the filtrate samples were collected for analysis in order to leach the membrane and eliminate possible water soluble contributions from the membrane filter (66,71). In order to eliminate the adsorption of trace metals from the 0.05 μm membrane-filtered sample and to minimize complex formation, ultrapurified nitric acid was added to the sample to about pH 1 - 2. This acid-preserved sample was stored in a refrigerator and protected from light until time of analysis.

64.   Nutrient samples were usually analyzed immediately after sampling. If prompt analysis was impossible, the nitrogenous species were acidified with sulfonic acid (100 μl in 100 ml sample) and stored at $4^{\circ}C$ (72). Samples for

orthophosphate and total phosphorus were quick-frozen at 0°C (73) and the dissolved silica samples were acidified with 0.3 ml of 1.0M HCl in 100 ml samples (74).

Extraction and Characterization of Organic Substances

65.   The sediment samples were shaken with 0.1M NaOH on a Burrell "wrist-action" reciprocating shaker for 4 - 6 hrs at room temperature under a nitrogen atmosphere to prevent oxidation. The samples were then rapidly centrifuged at 10,000 rpm on an IEC B-20A high speed centrifuge. The solid remains were repeatedly extracted until the supernatant became virtually colorless. This usually took 4 or 5 one-liter 0.1N NaOH extractions. All of the supernatant solutions from the successive extractions were then combined. The combined supernatants were acidified with 3N HCl and left to stand for 48 hrs. The fulvic acid (supernatant) was separated from humic acid (precipitate) by centrifugation at 20,000 rpm (51).

66.   Each sediment was analyzed in three fractions for organo-metallic interaction:

   a. $TO(NaOH)_{sx}$--total organic carbon contents obtained through successive extractions with 0.1N sodium hydroxide solution
   b.   Humic acid
   c.   Fulvic acid

The humic acid precipitate was dissolved back into 0.1N NaOH in which trace metal content was determined. No effort was made to remove carbonates by HCl prior to extraction with 0.1N NaOH because of the possible loss of trace metals attached to organic matter. The humic acid pellet was not dialyzed (purified), in order to preserve the humic acid-trace metal complex; however, the harsh extraction

procedure may have already altered the nature of these complexes.

67.   Total organic carbon determinations were performed on the sediment using a Leco TC-12 Automatic Carbon Determinator. Prior to analysis, all samples were treated to remove carbonates (75). Total organic carbon analysis on liquid samples of $TO(NaOH)_{sx}$, humic acid, and fulvic acid was performed on a Beckman TOC Analyzer equipped with flame ionization detector.

Analytical Methods

68.   pH, dissolved oxygen, total dissolved sulfide, and temperature were measured according to procedures described in Standard Methods (76). Slight modification was made on the methylene blue photometric method for total dissolved sulfide, which was then checked by the sulfide electrode method.

69.   The analytical methods for trace metals, nutrients, chlorinated hydrocarbons, and particle size are listed as follows.

Trace metals

70.   A Perkin-Elmer Atomic Absorption Spectrophotometer Model 305B with flame and graphite atomizer Model 2100 and deuterium arc background corrector was used for the metal analysis. The analysis of trace metals in seawater presented problems due to:

    a.   low concentrations present
    b.   presence of interfering ions
    c.   contamination
    d.   adaptability to multi-element determination
    e.   reduction of sensitivity due to matrices present
    f.   difficulty in preparation of standards

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71. Trace metal analysis in seawater is obviously very complicated. In this study, a combination of methods (77-81), together with some modifications, was used to obtain the most effective method of analysis. Following is a brief summary of the methods adopted:

	Method	Elements
1.	Direct injection	Cr, Fe, Mn
2.	APDC-MIBK extraction	Ag, Cd, Cu, Ni, Pb, Zn
3.	Flameless atomic absorption	Hg

72. The concentrations of chromium, iron, and manganese in the seawater samples were high enough to be injected directly into the graphite furnace and still obtain good response, provided the deuterium arc background corrector was used to lessen interference from volatile salts during atomization. The absorption due to sodium chloride is shown in Figure 4 (69). The other elements were not amenable to direct injection, due either to low concentration or to light scattering effects, so the APDC-MIBK extraction method was necessary. This method involves the complexation of metal with ammonium pyrolidine dithiocarbamate (APDC) and extraction of the metal-APDC complex into methyl isobutyle ketone (MIBK). This step is advantageous since it concentrates the metals to a level within the detection capability of the AA spectrophotometer, and separates the metals from the interfering salts that are present. Many of the heavy metals strongly complex with APDC over a wide pH range (2.5 - 7.0) (82). Mercury was rendered volatile and released by sparging nitrogen gas, then measuring its absorption on the AA spectrophotometer.

73. APDC-MIBK extraction--One hundred ml of the acidified sample is taken, and the pH adjusted with NaOH to 2 - 5, depending on the element to be determined. Five to seven ml of MIBK and 1 ml of 1% APDC (previously shaken

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with equal amounts of MIBK and separated) are added, and equilibrated on a Burrell wrist shaker Model 75 for 20 - 30 minutes. The sample is transferred to a separatory funnel, saving the lower aqueous layer for standard preparation and the upper MIBK layer for subsequent analysis. To prepare the standards, 500 ml of extracted seawater is subjected to another extraction using 25 ml of MIBK and 5 ml of 1% APDC to remove any trace of heavy metals. This is shaken vigorously and the layers separated in a separatory funnel. Several 100-ml portions from the seawater layer are taken and increasing increments of stock standard solutions are added. Procedure continues as described above, using 3 to 5 ml of MIBK (solubility of MIBK in seawater approximately 2% at room temperature) and 1 ml of 1% APDC for each 100 ml standard volume. The MIBK extracts are then injected with an Eppendorf micropipette into the graphite furnace of the AA spectrophotometer. The absorbances from the samples are compared with those of the known standards. Absorbance outputs were recorded on a Perkin-Elmer 56 recorder which has a scale expansion to improve recorder readout.

74. Preparatory AA spectrophotometer work--Numerous hours of preliminary work were devoted to obtaining optimum operating conditions on the Perkin-Elmer AA spectrophotometer. For direct-injection analysis, most of the major seawater salt is removed during charring at a temperature of approximately 1250°C. The small amount of salt left can be compensated for by using the deuterium arc background corrector. Since the volatile temperatures of silver, cadmium, lead, and zinc are lower than those of the salts, direct injection cannot be used for these elements. Slight modifications were necessary on settings for the APDC-MIBK extracts over those recommended in "Analytical Methods for AA Spectroscopy using the HGA Graphite

Furnace" (83). The settings, especially for charring and atomizing temperatures and times, were very sensitive for some elements, so that a slight adjustment resulted in major changes in absorption peak characteristics. To get a uniform peak response, sample injection size was kept at 10 µl.

75. Based on experience during this study, the optimum settings used in trace metal analysis are listed in Table 3. The APDC-MIBK complexes for some elements are stable for a limited time only, so the following order for analysis of the individual elements was followed: zinc, cadmium, nickel, lead, silver, and copper. The time factor is very important and should be seriously considered in order to obtain reliable data.

76. Variation--The coefficient of variation of replicate injections in the determination of trace metals using the graphite furnace atomizer was within 1 - 5% for most of the metals, with the exception of Cd, which was found to be in the range of 5 - 10%. The percentage of recovery from known additions of trace metals to sediment using the acid digestion procedure was between 92 and 104%. The lower percentage of recovery was obtained for Cd and Pb, whereas Fe showed the highest percentage of recovery.

Nutrients

77. Organic nitrogen (Kjeldahl method) and dissolved silica (heteropoly blue method) were analyzed according to Standard Methods, 13th Ed. (76). Ammonia and nitrite were determined by the methods outlined by Riley, et al. (74). Nitrate was determined by the modified Brucine method (84). Orthophosphate and total phosphorus were determined by the amino-naphthol-sulfonic acid method (85).

Chlorinated hydrocarbons

78. The extraction, separation, and identification

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Table 3

Optimum Operating Conditions for Trace Metal
Analysis with the AA Spectrophotometer

| Trace Metals | Wavelength Å | Optimum Operating Conditions* | | | | | |
| | | Drying | | Charring | | Atomizing | |
		Temperature, °C	Time, sec.	Temperature, °C	Time, sec.	Temperature, °C	Time, sec.
Ag	328.1	125	20	650	30	2400	8
Cd	228.8	125	30	400	30	1500	8
Cr	357.9	125	30	1250	45	2600	6
Cu	324.7	125	20	950	30	2550	8
Fe	248.3	125	20	1250	60	2400	7
Hg	253.7	--	--	--	--	--	--
Mn	279.5	125	20	1100	60	2400	5
Ni	232.0	125	20	1200	40	2550	7
Pb	283.3	125	30	550	40	2000	7
Zn	213.9	125	30	500	50	2000	6

--not determined

* 10 µl sample size, MIBK background

of chlorinated hydrocarbons were performed in accordance with the published literature (86-93). The details of the operation are described as follows.

79. Extraction--Ten g of undried sediment was weighed into a 500-ml Erlenmeyer flask with ground glass stopper, while another 10 g of sediment was weighed to determined moisture content. To this flask was added 250 ml of aceto-nitrile (pesticide quality, Mallinkrodtt). The flask was then shaken for 1 hr on a reciprocal shaker. The sample was kept in a constant temperature chamber ($14 \pm 2^{o}C$) overnight. Next, the sample was again shaken for 2 hrs and filtered through 5 g of Celite (Celite 545, Sargent Welch) media on Whatman No. 4 filter paper under mild vacuum. At this time another 100 ml of acetonitrile was added to avoid the possible loss of chlorinated hydrocarbons on the flask wall, Celite, or residue. The filtrate was transferred to a 500 ml Kuderna-Danish concentrator and concentrated to 5 ml on a water bath. The concentrated extract (filtrate) was then transferred to a 1000-ml separatory funnel con-taining 200 ml of double-distilled water and 10 ml of satu-rated aqueous NaCl. Eighty ml of petroleum ether (pesti-cide quality) was used to clean the concentrator, and was then added to the separatory funnel. The funnel was shaken by hand for 5 min and then kept still until clear separa-tion of phases occurred. The aqueous phase (bottom layer) was drained into another separatory funnel containing 80 ml of petroleum ether for the second extraction. After the third extraction, the aqueous phase was discarded and all petroleum ether extracts collected into a Kuderna-Danish concentrator. After the petroleum ether extract was con-centrated to approximately 5 ml, it was then eluted on the prepared activated florisil column.

80. Florisil column elution--A chromatographic tube

(450 x 28 mm) with a removable frittered glass and Teflon
stopcock was packed with 15 g of activated florisil (60/
100 mesh, G.C. grade) and topped with 15 g of anhydrous
sodium sulfate (analytical grade, Mallinkrodtt). The col-
umn was then washed with 70 ml of petroleum ether. The
petroleum ether extract (concentrated) was added when the
petroleum ether wash sank through the top surface of the
anhydrous sodium sulfate. Elution was then carried out,
first with 175 ml of petroleum ether (0% E.E. = 0%v ethyl
ether + 100%v petroleum ether; 6% E.E. = 6%v ethyl ether +
94%v petroleum ether; and 15% E.E. = 6%v ethyl ether + 85%v
petroleum ether); next with 100 ml of 6% E.E.; and finally,
with 150 ml of 15% E.E. During elution, flow rate was con-
trolled by the stopcock at approximately 2 ml/min. With
this florisil column elution, PCB's and most of the DDE
were recovered in 0% E.E.; most organochlorine compounds
in 6% E.E.; and Endrin and Dieldrin in 15% E.E. The eluted
sample was again concentrated and the exact volume was
measured.

81. Since sulfur was present in relatively large
amounts in every sediment sample tested, every extract was
treated with mercury to remove sulfur before injection into
the gas chromatograph.

82. <u>Identification and quantification</u>--The purities
and suppliers of standard solutions of chlorinated hydro-
carbons used in this study are more than 99%. DDT series
were obtained from Supelco, PCB's from Monsanto, and Diel-
drin from Shell Chemical. A Hewlett-Packard Research Gas
Chromatograph Model 5750 equipped with a Ni^{63} electron
capture detector was used throughout the study. The glass
column (1220 x 4 mm) was packed with 5% QF-1 (Chromosorb
W-HP, 80/100 mesh, Sargent Welch). The carrier gas was
95% argon and 5% methane.

83. The sample components were identified by compari-
son of retention times of unknown peak to the known peaks
of reference standard solutions, and were quantified by
comparison of the peak height of the identified component
to the peaks of the component in the reference standard
solution. In the earlier stages of this study, difficul-
ties were encountered in the quantification of some com-
ponents with close retention times, mainly in the 6% E.E.
eluted samples; for example, in the quantification of
o,p'DDD and o,p'DDT, or p,p'DDD and p,p'DDT. Therefore,
in addition to the single component reference standard
solutions, multicomponent solutions with different com-
binations of concentrations and components were prepared.

84. Preliminary sample injections were always per-
formed to decide whether further concentration or dilution
of the sample would be required, and to judge which series
of reference standard solutions should be used.

85. Extraction efficency--The recovery efficiencies
of pesticides from spiked samples from this study in com-
parison with those of other workers in recent publications
(94,95) are listed in Table 4. In this study, only two
consecutive petroleum ether extractions were performed,
while three extractions were used for sediment samples in
other studies.

Table 4

Recovery Efficiency of Chlorinated Hydrocarbons
from Marine Sediments

Pesticide	Recovery efficiency, %		
	A	B	C
p,p'DDE	86-94		96
o,p'DDE	81-91	97.1-99.5	--
p,p'DDD	87-97		97
p,p'DDT	85-99	97.6-100	--

Table 4, Concluded

Pesticide	Recovery efficiency, %		
	A	B	C
p,p'DDT	86-94	97.2-100	89
o,p'DDT	85-98		90
Dieldrin	85-94	--	91
PCB's	93-102	--	--

A = this study

B = Goerlitz and Law, Reference 94

C = Woolson, Reference 95

Particle-size analysis

86. The sediment sample was pretreated with 30% H_2O_2 to remove organic matter, using 6 mg/l of sodium hexameta-phosphate $(NaPO_3)_6$ (J.T. Baker Chemical Co.) solution as a dispersing agent. After wet-sieving the sample using US STD No. 230 sieve, the particles of the fine fraction ($\leq$62 µm) were further analyzed in accordance with the pipette method (96).

PART IV: RESULTS AND DISCUSSION

Characterization of Sediments

87.   The sediments under study were classified into
silty clay, sandy silt, and silty sand from the particle
size data (Table 5). Trace metal analyses were performed
for cadmium, chromium, copper, iron, lead, manganese, mer-
cury, nickel, and zinc. Total metal contents and the gen-
eral characteristics of the sediments are given in Tables
6 and 7. For each metal, the reported number is the aver-
age of three separate analyses determined on three sediment
samples from the same location. In the different types of
sediment, it was found that the trace metals content de-
creases with increasing sand content. The interstitial
water analyses of each sediment for trace metals are given
in Table 8. Because some phases of study lagged behind
due to very difficult experimental situations, some data
are not complete; for example, Station 7 was only consi-
dered in the latest part of the study.

88.   The results of the sequential selective chemical
treatment of different types of sediment are given in
Tables 9 - 12. Each number represents the average of analy-
ses from two separate chemical treatments of different
sediment samples from the same location. In most cases,
the sum of the sequential extractions of trace metals
falls within ±10% of the gross trace metal analysis. Only
in a few cases does it exceed 30%, but in the case of cop-
per in one sediment sample it was found to deviate as much
as 80%.

89.   In sequestering trace metals from the organic and
sulfide extractions, a larger fraction of trace metals was

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leached when the sediment was oxidized with hydrogen peroxide and extracted with 1.0M ammonium acetate solution at about pH 2, in comparison with an extraction with 0.01M nitric acid. Lead was found to show substantial difference between the two extractions. Adsorption of leached trace metal ions by active sites in the oxidized sediment may be the reason for a diminished extraction by 0.01M nitric acid solution, whereas with an ammonium acetate extraction at about pH 2, the adsorbed trace metal ions on active sites were exchanged with ammonium ions in solution. It may also be that ammonium acetate at pH 2 is a stronger extractant than 0.01M HNO_3. Only the method using H_2O_2 oxidation and extraction with 1.0M ammonium acetate at approximately pH 2 is considered in discussing the partitioning of trace metals to the organic and sulfide fractions of harbor sediments.

90. The combined acid reducing agent (which consisted of a solution of 0.04M hydroxylamine hydrochloride in 25% acetic acid) leached more of the trace metals associated with micronodules than did a sodium dithionite-citrate extract. The attack of the combined acid reducing agent on the lattice structure of the clay minerals has been ruled out. Chester and Hughes (5) indicated that the structure of clay minerals would remain intact. They further reported that it would also effectively dissolve almost all the iron and manganese oxide phases from ferromanganese nodules. Therefore, the trace metal values obtained with the combined acid reducing agent are more meaningful in terms of the association of trace metals with micronodules. The lower amounts of trace metals extracted in dithionite-citrate extract could be attributed to a higher pH value (around 7) in the extractant, and different degrees of complexing ability of citrate ions with various

trace metals. Also, the recrystallization of dithionite
before usage may have caused the loss of some reducing
power.

91. The trace metal contents of the different geo-
chemical fractions in different types of sediment are
listed in Table 13. The third column in Table 13 repre-
sents the sum of the trace metal fractions extracted in
successive selective chemical treatments. The existence
of trace metals of different origins in the sediment are
reported as percentage fractions of the sums found in
Column 3. The non-residual components represent the frac-
tions derived from natural weathering processes and man-
made pollution. The results for individual elements are
discussed separately in the following sections.

Cadmium

92. The total cadmium concentration of the sediment
varies between 0.66 and 2.2 ppm. No cadmium content was
detected in the soluble form and ion exchangeable phase.
Table 13 indicates that between 86 and 97% of the total
cadmium content in the sediments is derived from external
sources, pollution or marine-derived, in contrast with
those of mineral crystalline structure--the "residual"
portion, soluble only by destruction of the crystal lat-
tice. The natural background levels of cadmium in the
San Pedro Channel range from 0.6 to 1.0 ppm (97).

93. The distribution of cadmium in the hydrogenous
fractions of sandy silt and silty clay were similar. The
large majority of cadmium was associated with the nodular
portion with only a minor fraction in the non-nodular part.
By contrast, the distribution of cadmium between the nodu-
lar and non-nodular portions of the silty sand sediments
was more nearly equal, with a somewhat larger fraction in
the non-nodular part. In general, as the sand content of

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the sediment increased, a larger percentage of hydrogenous
cadmium was associated with the non-nodular hydrogenous
phase and a lower percentage was associated with the micro-
nodules. Between 12 and 44% of the non-residual (including
land source contamination and marine-derived) cadmium was
bound with organics and sulfides. The percentages of land
source pollution and marine-derived cadmium in the sulfide
and organic extracts are found to increase as the sulfide
content in the sediment increases, as shown in Figure 5.
An average of 8% of the total cadmium content in marine
sediments is of lithogenous origin, as can be seen in
Table 13.

Chromium

94. The total chromium concentration in the sediment
varies between 67 and 178 ppm. Table 13 shows that between
26 and 40% of the total chromium is either from land source
pollution or of marine derivation. Between 4 and 11 ppb of
chromium was detected in a soluble form in the water ex-
tract, whereas 2 to 16 ppb of chromium was available in
the ion exchangeable form.

95. Between 75 and 88% of the non-residual chromium
is associated with the micronodules and clay coating. It
clearly indicates that most of the land source contamina-
tion and marine-derived chromium is incorporated either in
ferromanganese nodules and iron oxides in the sediments
or as coating on clay particles. About 8% of the non-
residual chromium was associated with the organics and sul-
fides. These findings are similar to those reported by
Chester and Hughes (10), in that most of the authigenic
chromium is located in the micronodules and non-nodular
hydrogenous phases. The lithogenous contribution to the
total chromium content varies between 60 and 74% in the
different types of sediment. This percentage is similar

to that reported by Chester and Messiha-Hana (11).

Copper

96. The gross concentration of copper in the sediment
varies between 35 and 568 ppm. High copper content was ob-
served in the silty clay sediment. In general, the sum of
the copper extracted in the various individual successive
treatments showed a close agreement with the total copper
obtained. However, in silty clay sediment the difference
amounted to as much as 80%. No copper was detected in the
water extract and ion exchangeable form (ammonium acetate
extract) as shown in Tables 9 - 12. The study by Nissen-
baum (4) also showed that copper was absent in the water
extract.

97. Table 13 indicates that between 12 and 32% of the
total copper is non-residual, except in the case of silty
clay sediment, which shows only 1.5% to be of non-residual
origin. Nodular and non-nodular hydrogenous fractions of
non-residual copper showed a great deal of variance among
these different types of sediment. Nonetheless, an average
of 90% of the non-residual copper was associated with the
micro nodules and non-nodular hydrogenous fraction. The
percentage of non-residual copper in the organic and sul-
fide materials (biogenic) was found to increase with in-
creasing concentrations of sulfide in the different types
of sediment, as shown in Figure 5. The majority of the
copper content, between 68 and 98%, is apparently of lithog-
enous origin in these sediments. These findings are in
close agreement with those made by Chester and Hughes (10),
but differ significantly from the findings of Nissenbaum
(4), who reported that 10 - 14% (1 to 8 ppm) of total cop-
per was found to be associated with silicate minerals in a
sediment core from the Sea of Okhotsk.

Iron

98. No soluble iron was found in the distilled water extract. An average of 36 ppm of iron was associated with the exchangeable ions in the sediments, but no correlation with sediment types was observed. Table 13 indicates that between 18 and 26% of the total ion is non-residual material. This iron would be chelated by organics, appear as sulfides, micronodules, and iron oxide, or be adsorbed on the surfaces of other minerals. Around 7 - 11% of the non-residual iron is incorporated with organic solids and sulfides (biogenic fraction).

99. In sandy silt and silty clay sediments, 43 to 51% of the non-residual iron is associated with the micronodules. This fraction increases to 59 and 69% in silty sand sediment. The non-nodular hydrogenous iron in sandy silt and silty clay sediment was between 40 and 50% of the non-residual iron, and between 20 and 30% in the case of silty sand sediments. The higher percentages of the non-residual iron associated with non-nodular hydrogenous origin could be the result of iron precipitation from seawater to be incorporated into the sediment, as indicated by Goldberg and Arrhenius (98), or coating on soil particles from land sources. Most of the iron in the present study is not leached by the successive selective chemical treatment. Between 74 and 82% of the total iron was of lithogenous origin in deep sea sediments.

Manganese

100. The total manganese content in the sediment varies from 380 to 490 ppm. Between 1 and 2 ppm of the manganese is in the ion exchangeable form. Incomplete dissolution of manganese in micronodules was observed on these sediments using selective extraction of manganese oxides with acidi-

fied hydroxylamine hydrochloride, using Chao's method (6).
Later extraction with combined acid reducing agent at
100^OC releases substantial amounts of manganese in almost
every case.

101. Between 17 and 25% of the total manganese is non-
residual, and of this, Table 13 shows that 50% is associa-
ted with micronodules, while non-nodular manganese ac-
counts for 35 to 41%. The reason for the relatively high
amount of non-nodular manganese leached into dilute acetic
acid could be the presence of manganese carbonate and MnO_4
in the sediments; no correlation between the percentage of
carbonates and non-nodular hydrogenous manganese was ob-
served. This may also imply that much of the manganese
exists as simple oxides or oxide coatings. From 13 to 17%
of the non-residual manganese is associated with organics
and sulfides. Between 75 and 83% of the total manganese
content is held in the lattice structure of clay and sili-
cate minerals.

102. The observed trends of various geochemical forms
of manganese in Los Angeles Harbor sediments differ tre-
mendously from those reported by Nissenbaum (4), Chester
and Hughes (10), and Chester and Messiha-Hana (11), on
pelagic sediments. Those studies report that 68 to 88% of
the total manganese was marine-derived, and 12 to 32% was
of lithogenous origin; while this study shows that about
20% is non-residual and about 80% is of lithogenous origin.
This difference may be explained by the relatively short
residence of the harbor sediment in comparison with that of
pelagic sediments.

Nickel

103. The total nickel content of the sediments varies
from 18 to 47 ppm. Between 7 and 10 ppb of nickel was de-

tected as a soluble form in the water extract. An average
of 25 ppb of nickel was found in the ion exchangeable
phase. Table 13 indicates that an average of 37% of the
total nickel is non-residual, and 60% of this fraction was
incorporated into the ferro-manganese nodules. Most of
the non-residual nickel is associated with micronodules,
non-nodular hydrogenous material, and coating on clay par-
ticles. Thus, the results indicate that a large fraction
of nickel is removed from the marine environment by the
scavenging action of iron and manganese oxides and hydrox-
ides, or transported by clay particles from land sources.
The average lithogenous content of nickel (63% of the to-
tal) in these shallow water sediments is in close agreement
with the values (55%) reported by Chester and Messiha-Hana
(11), but differ significantly from the results of Chester
and Hughes (10) on the deep sea sediments. About 20 - 25%
of the non-residual nickel was bound to organics and sul-
fides, but no pattern was observed between the percentage
of non-residual nickel in H_2O_2 extract and TOC or sulfide
concentration.

Lead

    104. The total lead content of the sediment varies from
32 to 332 ppm. Between 52 and 65% of the total is non-
residual. This is similar to the findings of Chow and
Patterson (99), who concluded that about two-thirds of the
lead in the pelagic sediment was associated with non-
residual minerals. Chester and Hughes (10) showed that an
average of 20% of the total lead is associated with micro
nodules and non-nodular hydrogenous origin. An average of
6 ppb of lead was available as soluble ion, whereas in
general no lead content was detected in the ion exchange-
able form, except in one of the silty sand sediments. This
sediment shows 12 ppb of lead in the ion exchangeable form.

It has been indicated that lead and copper are difficult to displace as an exchangeable form from the clays (100).

105. Between 63 and 76% of the non-residual lead is associated with micronodules. A large difference in the lead content associated with non-nodular hydrogenous origin together with the sulfides and organics was noted. In general, the percentage of non-residual lead associated with sulfide and organics was observed to increase with increasing sulfide content as shown in Figure 5.

Zinc

106. The total zinc content in the sediments ranges from 94 to 612 ppm. A high zinc content was obtained in the silty clay sediment. In general, the sum of the zinc extracted in the various individual successive chemical treatments agrees within ±10% with that of the separate analyses for total trace metal content.

107. An average of 135 ppb of zinc was found to be available in the ion exchangeable form in the silty sand sediments, whereas an average of 10 ppb of zinc was obtained in the silty clay and sandy silt sediments, as shown in Tables 9 to 12. Table 13 indicates that between 58 and 77% of the total zinc was non-residual. From 42 to 53% of the non-residual zinc is associated with the ferro-manganese nodules and 10 to 50% with non-nodular hydrogenous materials. About 13 to 37% of the non-residual zinc was found to be associated with organics and sulfide. The percentage of the non-residual zinc in the organic and sulfide extracts is found to increase as the sulfide concentration in the sediment increases, as shown in Figure 5. The zinc content of lithogenous origin was found to be between 23 and 42% of the total zinc.

108. In determining the pollution potential of a sedi-

ment, it is essential to differentiate between the availability and nonavailability of trace contaminants to the biota. It is speculated that land sources pollution and marine-derived trace metals are regarded as potentially available for release to the water column over a long period of time, while those contained in the crystalline structure of minerals are considered to be unavailable for biological uptake under normal conditions. In this study, it has been found that the non-residual fraction can range from as high as 98% for cadmium to as low as 1.4% for copper. It is important that such information be available for determination of the pollution potential of sediments.

109. Among the various geochemical fractions of the sediment, trace metals in interstitial water and in the water soluble phase are indicative of the amounts which may be immediately released upon resuspension or disturbance of the sediment. The data presented in this paper show that this portion represents an extremely small fraction of the total available trace metals. The remaining portion of the non-residual fraction represents the reservoir of trace metals available for potential release if significant changes occur in the environmental conditions of the overlying waters or sediments.

110. A close examination of particle size and gross concentrations of contaminants (Tables 5 and 7) indicates that sediments containing more than 20% clay substances (<5 μm) generally contain TOC, chemical oxygen demand (COD), and trace metal contents far above those of sediments with less clay. However, this is not reflected in the concentrations of trace metals in interstitial waters.

Effects of Dispersion and Settling on
Water Quality

111. Results of the individual trace metal and nutri-
ent analyses of the 0.2 µm filtered samples are tabulated
as a function of time in Tables 14 - 37. Concentrations of
trace metals in original seawater are included for the pur-
pose of comparison of the release of trace metals and nu-
trients within each sediment type. Discussion of effects
and reactions will be limited to major mechanisms, due to
the wide diversity and complexity of seawater-sediment
interactions.

Dissolved oxygen

112. Upon addition of the sediment-seawater mixture
(1:4) to the seawater column, the D.O. immediately drops
to a much lower level with organic-sulfide rich sediment
than with sandy type sediments. As seen in Table 38, some
type A and C tests recovery slightly with time, while test
types B and D virtually drop to zero due to the high ini-
tial oxygen demand of the sediments (test types are de-
scribed in Table 2). Continual bubbling of compressed air
(type E) permits the D.O. to recover to its original con-
tent within 2 - 4 hours. An increase in the seawater-to-
sediment ratio subsequently prevents the abrupt initial
drop in dissolved oxygen.

113. In the presence of oxygen, the lower outputs of
soluble iron indicate the oxidation of iron to the insolu-
ble species of hydrous ferric oxides. The presence of oxy-
gen determines the chemical form of many of the elements,
ultimately influencing the migration of their ions. The
oxidation of sulfides may be accelerated considerably in
the presence of transition metals as catalysts (101). The
presence or absence of dissolved oxygen has been used as
the bases for predicting redox condition, inasmuch as Eh

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measurements represent the measurement of mixed potentials
rather than reflecting the actual reaction.

Temperature and pH

112. All column tests were performed at room tempera-
ture. The seawater temperature fluctuated between 1 and
$2^{\circ}C$; no observable effect can be directly attributed to
the small temperature change. Temperature change generally
affects the solubility of metals as well as silica. How-
ever, variations in the range of $20 \pm 5^{\circ}C$ will not affect
the equilibrium to a large extent. Variations in pH are
insignificant in all cases.

Sulfide

113. Column tests using silty clay sediment (Station
6) gave the highest release of sulfide, with the quiescent
tests releasing more than the agitated tests, or the
transfer of oxygen into the container due to agitation
resulting in the oxidation of sulfide. The presence of
sulfide would create a reducing environment; upon oxida-
tion, the conversion to sulfate results in lowering the
pH of the solution.

Trace metals

114. Most of the trace metals displayed a release
pattern immediately after the addition of the sediment
mixture to the seawater. A sudden release of metal to the
seawater during the first hour was followed by subsequent
removal from solution; either gradually, as often found in
slightly reducing environments, or immediately under
slightly oxidizing environments. The initial release is
most likely due to the dilution of interstitial waters,
dissolution of the solid phase through complex formation,
and release from the exchangeable phase. With moisture
contents of 26 to 43%, at a dilution ratio of 1:20, a

50-fold increase for soluble iron, 5-fold increase for manganese, and 1.5 to 3-fold increase for nickel and zinc should be observed due to the release of interstitial waters (see Table 8). It is apparent from the data presented in Tables 14 to 37 that the release from interstitial waters alone is not enough to account for most of the release. Complex formation and ion exchange seem to account for the bulk of the release. Similar phenomena were observed in the mixing of sewage sludge particulates with seawater (102).

117. During the resuspension of sediments in seawater, numerous forms of interactions occur between ions, solution, and solid, or between a combination of two or more forms, resulting in a net transfer of metal ions through the sediment-seawater interface. The turbulent mixing during the introduction of the sediment mixture promotes the release and diffusion of the metals from the enriched interstitial water found in reduced sediments. Upon release and exposure to oxygen, many interactions occurred. Metal species can be readsorbed to organic matters (13,42, 103-105); hydrous iron and manganese oxides (13,42,105-111); precipitated into living organisms (42,106,110); or form complex compounds (13,42,107,110,112). Many of these phenomena probably explain the subsequent variations following immediate release. Active redox species such as carbon, nitrogen, oxygen, iron, manganese, and sulfur play predominant roles in regulating the soluble metal concentrations in the water column.

118. Although most of the metal species exhibited varying degrees of release from the sediment phase, the raw data do not show distinct patterns to provide a generalized trend for different types of sediment. Due to the limited dilution ratio available in the water column, which is

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quite small in comparison with the actual dilution available in open-water disposal, the concentrations of dissolved oxygen and sulfide are controlled to a great extent by the sediment characteristics. With the exception of continuous bubbling with air or dissolved oxygen, almost every type of experiment results in the complete depletion of dissolved oxygen within a very short period.

119. In the short-term study (48-hr period), the concentration factor (ratio of metal species in the water column to that of original seawater) for each metal species calculated from the areas on the time-concentration graphs enable the comparison of the relative degree of release for each metal. Table 40 tabulates the metal release factor for each metal and test type relative to the seawater background. The release phenomena of the trace metals may be classified into three groups. The metals most significantly released (factor >10) were iron, manganese, and nickel; while chromium, copper, lead, and zinc may be considered moderately released, with a factor of between 3.5 and 17.5. The release of silver, cadmium, and mercury was negligible. Some overlapping in the concentration factor cannot be avoided for such a simplified grouping scheme.

120. Changes in silver and cadmium concentrations were very slight under the various types of test conditions. The concentrations showed lower values with agitation and were very near the concentrations of the original seawater. Silver is not readily affected by adsorption. The low concentrations of these species in interstitial waters may partially explain the low level of release.

121. Chromium and copper, although moderately released (factor 6.5 ~10.9), demonstrated very little variation with change in redox conditions. Chromium concentration decreased slightly under oxidizing conditions while

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copper concentration increased under the same conditions. Chromium does not precipitate as sulfides, and under a strong reducing environment, the predominant form is the complex cation $CrOH^{+2}$. Copper under reducing conditions is generally less soluble, probably due to the ubiquitous presence of reduced sulfur species in sediments.

122. Mercury concentrations varied slightly under the various environmental conditions. The concentration was higher under oxidizing conditions than under slightly reducing conditions. Values from the type C experiments were high, indicating the possibility of contamination. Probable compounds formed in the oxidizing state are the halide species, namely $HgCl_4^{-2}$, $HgCl_2$, and $HgCl_3^-$; while under reducing conditions, bisulfide becomes the important controlling species.

123. The three metals showing the most significant change in concentration with change in redox condition are iron, manganese, and nickel. Their transport phenomena behaved similarly, and their order of release may be shown as follows:

reducing > slightly oxidizing > oxidizing
Ferrous constituents are generally more soluble than ferric constituents. The ratio of measured concentration to the original seawater concentration was 165 for quiescent reducing conditions, and 52 for agitated reducing conditions. Under oxidizing conditions, less soluble ferric oxides and hydroxides are formed, as shown by the lower release factor varying from 16 to 28 times over the seawater background.

124. Differences in release factors for manganese were very small. Under reducing conditions, the slightly higher release factor may be due to the appearance of appreciable amounts of the soluble Mn(II) compounds, which

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upon oxidation convert into the less soluble Mn(IV) compounds. The small difference between oxidizing and reducing conditions testifies to the fact that oxygenation of the Mn(II) species is very slow in the well-aerated seawater environment.

125. The release of nickel was relatively high. The nickel ion is strongly adsorbed by the hydrated oxides of iron and manganese. Under reducing conditions, nickel is not subject to the direct control of sulfide as it does not form the very insoluble sulfide in seawater. It can, however, be co-precipitated in a sulfide-rich environment with other metal sulfides.

126. The release of lead and zinc under quiescent conditions showed higher values under oxidizing than under reducing environments, with release factors ranging from 3.4 to 17.5. Under agitation, lead demonstrated a reverse trend, while zinc released to a higher degree, with concentrations under both oxidizing and reducing conditions of similar values. Zinc is highly vulnerable to contamination, which could be the possible cause for the high readings. Experiments by Krauskopf (106) showed that zinc and lead, as well as copper, strongly adsorb to surfaces such as ferric oxide, manganese oxides, clays, etc. These metals can also be readily precipitated as sulfides.

Freshwater sediments

127. Upon resuspension of freshwater sediments in both seawater and freshwater, the pH dropped slightly during the first few hours and ended a bit lower under oxidizing conditions (group A test), while the pH under slightly reducing conditions (group B test) recovered and showed a slightly higher value. Comparing the data obtained (Tables 14 to 37), freshwater sediments generally

released more soluble metals (based on averages) than marine sediments, except for iron. The soluble iron was very low in both cases. The release of manganese was exceptionally high, freshwater sediments showing a much higher release than seawater sediments.

128. During the experiment using freshwater sediment in seawater, a distinct brownish-yellow color appeared within 2 to 8 hours, starting from the seawater surface and gradually spreading downward. Freshwater sediments in fresh water did not produce any coloration in the water column. The mechanism of this phenomena cannot be explained at this time.

Nutrients

129. The raw data obtained from the column test samples for the nutrients were very irregular, making the observation of a characteristic release and/or uptake pattern for each nutrient, sediment type, or test type impossible. Some sort of generalization can be speculated, as the results indicate a varying degree of release of nutrients to the solution.

130. The addition of the water-sediment mixture to the water column causes the release of nutrients. The first 30 minutes showed a sudden release, followed by a slight decrease in nutrient concentration. After reaching an apparent equilibrium state, these concentrations stayed stable or varied to a slight degree only until the end of the experiment (48 hrs). Table 39 shows the group pattern for the individual nutrient.

131. Tests under reducing conditions (types B and D) generally exhibit a higher concentration level, with the agitated test (type D) having a higher value. Slightly oxidizing conditions (types A and C) assume a middle level

while type E (oxidizing) generally releases at a very low concentration level. In most of the tests, a sag in the concentration occurred between 2 and 8 hours. Silty clay (station 6) sediment released comparatively more nutrients than did the others, probably due to higher organic matter content or finer particle size. Sediment particles were observed to settle at a faster rate under aerobic conditions than in an anaerobic suspension, making filtration of the samples easier.

Table 39
General Characteristics of Nutrient Release

Nutrient	Initial Concentration, ppm	Peak Release, ppm	Trend after 8 hours
Ammonia nitrogen	0.04	0.15 - 0.36	slight or very slight upward
Organic nitrogen	0.15	0.40 - 0.86	slightly upward
Phosphate	0.025	0.30 - 0.88	steady or very slight downward
Silica	1.5	10.5 - 22.8	slight to medium upward

132. The release of ammonia and organic nitrogen leveled off to a constant value or gave a very slight upward trend by the end of the experiments, after the initial release and readsorption. The nitrogen release was greater for an anaerobic environment. The amount and form of nitrogen in solution phase is controlled to a large extent by the D.O. content. Under oxidizing conditions, the organic nitrogen as well as ammonium ions are oxidized to nitrite and subsequently to nitrate ions. Under anaerobic conditions, the Kjeldahl (soluble) nitrogen increased in concentration.

133. As shown in Tables 14 to 37, phosphate was released in large quantities under reducing conditions, es-

pecially in the organic-rich, sulfide-rich sediments. The
initial release of dissolved phosphate originates from the
interstitial waters as well as from sediment whose top
layer contains a high concentration of phosphate. The
greatest release of phosphate occurred in oxygen-deficient
waters. The release or precipitation of phosphate is asso-
ciated with and dependent to a great extent on the form of
the iron. Upon contact with dissolved oxygen, the ferrous
ion oxidizes to ferric ions, which subsequently react with
phosphate to form insoluble ferric phosphate according to
the equation:

$$Fe^{+3} + PO_4^{-3} \rightarrow FePO_4(s)$$
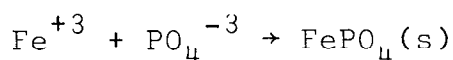
Under reducing conditions, ferrous iron is released and,
depending on the presence of sulfides, the Fe^{+2} ion may
form insoluble ferrous sulfide and release PO_4^{-3}, which
has a low solubility. The following equations show the
reactions:

$$FePO_4(s) + e^- \rightarrow Fe^{+2} + PO_4^{-3} \text{ (reducing condi-tion)}$$

$$Fe^{+2} + S^{-2} \rightarrow FeS(s)$$
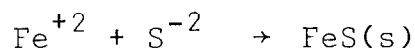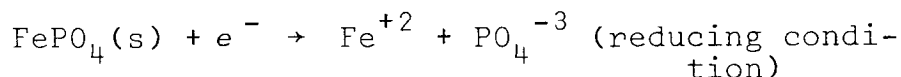
134. Dissolved silica in the interstitial waters is
generally enriched (113) and much more concentrated than
in the overlying water, as shown by the instantaneous up-
surge in concentration upon resuspension of the sediments.
Under aerobic conditions, silica behaves like the trace
elements by coprecipitating on the hydrated oxides of iron
and manganese (110). Under anaerobic conditions, the pre-
cipitate redissolves and releases the silicon into solu-
tion.

Long-Term Exchanges of Chemical Species
in Sediment-Water Interfaces

135. The exchange phenomena between sediment-seawater
interfaces differ widely under different environmental con-
ditions. Experimental data show that the direction of
transport of trace metals from sediment to seawater or
from seawater to sediment is controlled mainly by the re-
dox conditions of the overlying seawater, and the flux is
controlled chiefly by the type of sediment. Nutrients
were found to be released initially under all conditions.
As the contact time was increased, ammonia concentrations
were found to be decreased under oxidizing conditions,
while nitrate and nitrite disappeared under reducing con-
ditions. Concentrations of total phosphorus and ortho-
phosphate in the interfacial water were found to be re-
leased during the initial contact time, but were again de-
creased as contact time was increased. Soluble silica was
found to increase steadily. In general, concentrations of
trace metals in the interfacial waters were found to be at
the sub-ppb to ppb levels, while the concentrations of
nutrients were found to be in the sub-ppm to ppm ranges.
The amount of soluble chlorinated hydrocarbons was unde-
tectable even after 3 months of contact. The results of
the long-term effects of redox conditions on the transport
phenomena between different sediments are described as
follows.

Transport of Trace Metals

Cadmium

136. Figure 6 shows that cadmium can be significantly
released only under oxidizing conditions. Under oxidizing
conditions, the cadmium concentrations in the interfacial

water were increased about 15 times over the original sea-
water background levels (about 0.03 ppb) to about 0.5 ppb
after 4 to 5 months of contact. Under slightly oxidizing
conditions, there was no significant change in cadmium con-
centration. The concentration is close to the original
seawater background. Under reducing conditions, the cad-
mium concentration was at a very low level during the be-
ginning contact period (about 1 week). But when contact
time was increased, the concentration also increased.

137. No remarkable difference was noted among the
different sediment types under identical environmental con-
ditions. The silty sand sediment showed a spontaneous
release under both oxidizing and slightly oxidizing condi-
tions at the beginning of the contact period, followed by
a gradual decrease. When contact time is increased, the
trend of the exchange pattern tends to be the same. The
release of cadmium in the long-term experiment differs
greatly from the short-term release in the water column.
Due to the low enrichment factor of cadmium in interstitial
waters, the short-term release was insignificant in almost
every case. However, the large quantity of non-residual
cadmium in the sediment phase acts as a reservoir for re-
lease and reacts toward equilibria with overlying waters.

Copper

138. All types of sediment seemed to remove copper in
the beginning of the contact period (Figure 7). After one
day of contact, the release phenomenon was observed under
oxidizing and slightly oxidizing conditions. Under oxidi-
zing conditions, copper could be released to about 3 ppb
from silty sand sediment after 5 months of contact, to
about 2 ppb from silty clay sediment after 4 months of
contact. These concentrations are about 5 to 7 times high-
er than the original seawater background level (0.3 - 0.65

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ppb). The original copper concentration for background
seawater in the sandy silt sediment was very high (7.6 ppb).
But after contact, a spontaneous scavenging effect reduced
the copper concentration to around the same original back-
ground level as found for the other two sediment types.
When contact time increased, the copper concentration
again increased. The release rate of copper from sediments
took the following order:

silty sand > sandy silt > silty clay

139. Under slightly oxidizing conditions, the copper
concentration showed no significant difference from the
original background. Under reducing conditions, the copper
concentration was decreased to an extremely low level. Re-
dissolution of copper occurred, but at a very slow rate.
For instance, after 1 month of contact in the silty sand
test, copper was increased to around the original back-
ground level. Under the same environmental conditions,
the more clayey sediment is shown to release a lesser quan-
tity of copper than other types of sediment, even though
the copper concentration in the clay sediment is the high-
est. For the same type of sediment, the higher the oxygen
content, the higher the release rate. In both column and
long-term studies, the moderate release of copper repre-
sents the release of interstitial water and complex forma-
tion to a limited extent, with the overlying surrounding
seawater. However, the vast quantity of copper in sediment
does not constitute a reservoir for release. Instead, the
equilibria seem to be the controlling mechanism.

Chromium

140. The chromium concentration in the interfacial
water shows no significant change under any redox condi-
tion in all of the sediment types. The extremely slow

rate of oxidation of Cr(III) to Cr(VI) in the aerated sea-water environment explains the lack of redox effect. Also, the absence of chloride complex seems to limit any detectable release over the long term.

Iron

141. In general, iron was found to be released substantially from all types of sediment under reducing conditions, and to be released slightly under oxidizing and slightly oxidizing conditions. The order of the rate of release is:

reducing > slightly oxidizing > oxidizing

Under oxidizing conditions, the final concentrations were about 2 - 5 ppb (Figure 8; 120, 90, and 150 days for the silty clay, sandy silt, and silty sand sediment, respectively). But under slightly oxidizing conditions, the final concentrations could be raised to 10 - 15 ppb. Under reducing conditions, the release rate of iron was very rapid. For instance, the silty clay sediment may increase the iron concentration of the interfacial water from 0.5 ppb to about 100 ppb after 60 days of contact; the silty sand sediment may increase the concentration even faster than the silty clay, from 0.2 ppb to about 800 ppb after 60 days.

Mercury

142. A comparison of mercury release under different experimental conditions is shown in Figure 9. In general, the mercury concentration showed little change from the original seawater background concentration. Since the detected values were so close to the detection limit (0.02 ppb), the data seemed to be quite random. However, the following pattern was still observed:

oxidizing > slightly oxidizing > reducing

The final concentration of mercury under oxidizing condi-
tions was about 0.1 ppb. Like cadmium and copper, under
reducing conditions, the mercury concentration decreased
to a level below the detection limit. The concentrations
again increased after about 15 days of contact for silty
sand sediment and after about 2 months for the silty clay
sediment.

Manganese

143. The transport phenomena of manganese was similar
to that of iron under different environmental conditions,
following the release order:

reducing > slightly oxidizing > oxidizing

(Figure 10). Under the same environmental conditions, the
clayey-type sediment seemed to release less than the other
sediment types. The release of manganese under reducing
conditions was quite significant. For silty sand sediment
in the final concentration, the manganese concentration
was about 310 times that of the original background (0.25
ppb). For silty clay sediment, the concentration was
about 85 times that of the original 0.3 ppb. Under oxi-
dizing conditions, the final manganese concentrations were
less than 1 ppb in the silty clay and silty sand test, and
about 7 ppb in the silty sand test.

Nickel

144. In general, the concentration of nickel in the
interfacial water followed the order:

oxidizing > slightly oxidizing > reducing

(Figure 11). If enough contact time was allowed, the nick-
el concentration seemed to be higher under reducing condi-
tions than under slightly oxidizing conditions, as in the
silty sand test. In this experiment, the sandy-type sedi-

ment could release more nickel. Under oxidizing conditions, the final nickel concentration was about 6 ppb for sandy-type sediment and only about 2 ppb for clayey-type sediment. Like copper, in the reducing environment, nickel also showed deposition during a short contact period. The concentration increased again when contact time was increased. In the clayey type of sediment, the nickel can be scavenged to undetectable levels during the first week of tests; the nickel will then be gradually redissolved. The redissolution rate was quite high in the sandy sediments.

Lead

145. The transport phenomena of lead followed the same trend as cadmium, showing higher concentrations under oxidizing conditions (Figure 12). No significant change was observed under slightly oxidizing conditions, and a large decrease followed by a slight increase occurred under reducing conditions. Among these three conditions the concentration range is quite small, and the values never exceed sub-ppb levels even after 5 months of contact.

Zinc

146. Figure 13 shows that a fast release of zinc occurs after contact under both oxidizing and slightly oxidizing conditions. The clayey-type sediment could release more zinc than the sandy-type sediment. Under an oxidizing environment, the final zinc concentration was about 10 ppb for the clayey-type sediment and only about 3 ppb for the sandy-type sediment. For silty sediment, the final zinc concentration was about 5 ppb. Under slightly oxidizing conditions, the final zinc level was about 2 ppb in all types of sediments. Under reducing conditions, the zinc concentration decreased to a very low level at the beginning of the contact period and then increased again. Un-

der a reducing environment, the redissolution phenomenon for the silty clay sediment test was very clear. The concentration of zinc was even higher than that of the original seawater background after about 70 days of contact.

Silver

147. The amount of silver transported was undetectable (<0.02 ppb) under all conditions and in all types of sediment during the experimental period.

Transport of Nutrients

Ammonia

148. Under different redox conditions, ammonia was found to be released in the following order:

reducing > slightly oxidizing > oxidizing

(Figures 14 - 16). Among the different sediment types, ammonia was found to be released in the following order:

silty clay > sandy silt > silty sand

Under oxidizing conditions, the concentration of ammonia reached 0.7 mg/l for silty sand and sandy silt sediment, and about 4.5 mg/l for silty clay sediment, followed by a decrease and eventual disappearance after a few months of contact. Under reducing conditions, NH_3-N was found to be continually released to about 1 ~ 2 ppm for the silty and sandy sediments and to about 12 ppm for the clayey-type sediment.

Nitrite

149. Nitrite was present from about 10 days to 1 month of contact time in the presence of oxygen (Figures 17 - 19). With the exception of clayey-type sediment, the

NO_2-N was present in the ppb range. Under reducing conditions, nitrite was undetectable throughout the experimental period.

Nitrate

150. Nitrate was present in the interfacial water in the presence of oxygen (Figures 17-19). Under oxidizing conditions, the NO_3-N concentration in the silty sand sediment was about 0.5 mg/l; but in the silty clay sediment test, the NO_3-N concentration reached as high as 14 mg/l. Obviously, the concentration in sediment phase determines the rate of release to a great extent. However, after about 2 months of contact, the nitrate concentration decreased again. Under reducing conditions, the nitrate concentration was found to decrease constantly, until it reached an undetectable amount.

Organic nitrogen

151. For both silty sand and sandy silt sediments, the release of dissolved organic nitrogen was found to be higher under a reducing environment (Figures 14 - 16). Under oxidizing or slightly oxidizing conditions, the organic nitrogen content in the interfacial water of both sediments was found to decrease gradually to a trace amount. For silty clay sediment, under all types of environments, the organic nitrogen could be released to about 10 to 15 mg/l, or about 4 times that of the reducing environment in the silty sand test. After about 1 month of contact time, the concentration of organic nitrogen in the silty clay test decreased again. Under oxidizing conditions, the organic nitrogen was found to be decreased to zero.

Total phosphorus and orthophosphate

152. Concentrations of both total phosphorus and

ortho-PO$_4$ in the interfacial water rose steadily during the beginning of the contact period under all environmental conditions (Figures 20 - 22). As contact time increased, there was a decreasing trend in both total phosphorus and ortho-PO$_4$. In general, no significant differences in release amounts were found among all types of sediments. But the environmental conditions of the overlying water did affect the change, and followed the order:

reducing > slightly oxidizing > oxidizing

Dissolved silica

153. The dissolved silica was found to be released continuously during the entire experimental period, eventually reaching the concentration of 8 - 16 mg/l. For the sandy and silty sediments, it seems that a reducing condition can release more dissolved silica. For silty clay sediment, a reduction of soluble silica was observed, especially in the reducing environment, and some of the dissolved silica was removed from the interfacial water (Figures 20 - 22). A comparison of sediment types shows that the silty clay sediment has the highest release rate of dissolving silica, except under a reducing environment.

Transport of Chlorinated Hydrocarbons

154. The concentration of chlorinated hydrocarbons in the interfacial water of silty clay and silty sand sediments was analyzed over 3 months of contact time. The only species detected was PCB 1242, after 8 days of contact time in the silty sand sediment test. The reason for this detected PCB 1242 is unknown. The possibility of contamination is not ruled out.

Comparison of Experiments Under
Controlled and Uncontrolled Redox Conditions

155.   There was no marked difference between these
two types of experiments after redox effects were consid-
ered.   The concentrations of trace metals and nutrients in
the uncontrolled tests were close to those of the same
redox conditions in the controlled tests.   In the cases
of silty sand and sandy silt sediments, the final environ-
mental conditions of the uncontrolled test were close to
the slightly oxidizing condition of the controlled test.
For silty clay sediment, it was close to the reducing
condition.

Controlling Mechanisms for the Transport of
Trace Metals in the Sediment-Water Interfaces

Oxidizing conditions

156.   Most trace metals, with the exception of silver,
chromium, and mercury, were released under oxidizing
conditions.   The possible mechanisms for the increase of
soluble forms of trace metals in the interfacial water are:

a.   diffusion from interstitial water
b.   desorption from clay minerals or other solid
forms
c.   chemical reaction, i.e., oxidation of organics
and sulfides
d.   ion-exchange
e.   dissolution
f.   complexation
g.   biological actions

157.   In long-term experiments like this, physical and
biological effects are likely to be minor sources of solu-

ble trace metals. The main release phenomenon is probably caused by complex formation. From thermodynamic equilibrium calculations, it can be found that under oxidizing conditions the soluble species of trace metals may be tremendously increased from their free ion forms to complex forms (114-116).

158. The main soluble forms of cadmium may come from $CdCl_2^O$, $CdCl^+$, $CdCl_3^-$, and Cd^{+2} (114). In addition, the presence of carbonate, ammonia, and organic substances may form additional soluble complexes (44). This may explain the increase of Cd under oxidizing conditions.

159. The concentration of soluble mercury may also be controlled by chloride complexes ($HgCl_4^{-2}$, $HgCl_2^O$, and $HgCl_3^-$). But the release phenomenon of mercury was not quite as significant in this experiment. It may be very likely that the solubility of mercury was controlled by sulfides in the sediment. Despite the prevailing aerobic conditions in the water column the diffusion of O_2 from the water column in this quiescent system may have been too slow or unable to oxidize the high oxygen demand sediments beneath the surface. Due to the relatively slow reaction between mercuric sulfide and oxygen, the mercuric sulfide may remain the predominant solid phase in the sediment. Otherwise, the low concentrations of soluble mercury are not compatible with equilibrium calculations of chloride species.

160. Under oxidizing conditions, the soluble forms of copper in the interfacial water may be mainly controlled by ammonia, carbonate, and hydroxide. For lead, besides carbonate and hydroxide complexes, the chloride complexes also play an important role. For zinc, the main forms are probably Zn^{+2}, $ZnCl^+$, $ZnSO_4^O$, $ZnCl_2^O$, $ZnOH^+$, and $ZnCO_3^O$(aq).

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The Fe(II) and Mn(II) compounds are thermodynamically unstable under oxidizing conditions and oxidize to less soluble Fe(III) and Mn(IV) species. For this reason, the iron and manganese concentrations show no significant increase. The chromium concentration in the interface showed no significant change, probably as a result of the lack of soluble complexes and the low solubility of the hydroxide. A possible explanation for the undetectability of silver is the extremely low solubility of AgS and AgCl. Also, silver may be strongly adsorbed on sediments so that the release is too small to detect. The most likely explanation for the lack of silver release is the simple solubility consideration. Using a chloride concentration of 2% and a silver chloride solubility product of 10^{-10}, it can be shown that the saturated silver concentration under these conditions would be about 0.02 µg/l, the detection limit of the instrument.

161. The metal complexes which account for the high concentration under oxidizing conditions are not only from chloride, hydroxide, carbonate, or sulfate species. Others such as organo-complexes, ammonia complexes, etc., may also account for the soluble forms in this experimental system. Since most complex formation constants are lacking, especially organo-metallic complexes, and given the complexity of the experimental system, it is not possible to propose a fixed model with definite figures to explain the release phenomena.

Reducing conditions

162. In a reducing environment, with the exception of iron and manganese, most trace metals were decreased to an extremely low value at the beginning of the contact period. However, the concentrations of some of these metals (e.g., cadmium, copper, mercury, nickel, lead, and zinc) increased

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again as time passed. It is suggested that the deposition
effect during the beginning of the contact period is a
combined result of metallic sulfide formation and adsorp-
tion, because the metallic sulfide species are more stable
in comparison to most of the chloride, carbonate, or other
species. The subsequent increase of trace metals may be
primarily due to the following:

a.   formation of metallic sulfide complexes
b.   formation of organo-metallic complexes
c.   diffusion from interstitial water
d.   release of trace metals from the transformation
     of the highly insoluble hydrous metal oxides to
     the more soluble Fe(II) and Mn(II) compounds;
     and slow precipitation of metal sulfides due to
     kinetic effects

Among these factors, the equilibria of sulfide species may
be the most important factor in determining the metal con-
centration in the interface for several species. On the
other hand, organo-metallic complexes may play a role in
cases where soluble concentrations exceed equilibrium
calculations of metal sulfide complexes.

163. According to the stability constants from Ste-
Marie, et al.(117), Barnes and Czamanske (118), Schwarzen-
bach and Widmer (119), Anderson (120), and Sillen and
Martell (44), solubilization of metal species may be shown
as follows, if the metallic sulfide is the controlling
solid phase:

$$Ag_T = \left(\frac{K_{so}}{\alpha_2 \Sigma S_D}\right)^{\frac{1}{2}} \left[1 + K_2 K_1 (\alpha_1 \Sigma S_D)^2 + K_1 (\alpha_1 \Sigma S_D)\right] + 2K_{so2}(\alpha_1 \Sigma S_D)^2$$

$$Cd_T = \left(\frac{K_{so}}{\alpha_2 \Sigma S_D}\right) + K_{s10}(\alpha_0 \Sigma S_D) + K_{s11}\alpha_0 \alpha_1 (\Sigma S_D)^2 + K_{s12}\alpha_0 \alpha_1 (\Sigma S_D)^2$$

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$$Cu_T = \left(\frac{K_{so}}{\alpha_2 \Sigma S_D}\right) + K_{s12}\alpha_0\alpha_1(\Sigma S_D)^3$$

$$Hg_T = \left(\frac{K_{so}}{\alpha_2 \Sigma S_D}\right) + K_{s11}\alpha_0\alpha_1(\Sigma S_D)^2 + K_{so2}(\alpha_1 \Sigma S_D)^2 + K_{s20}(\alpha_0 \Sigma S_D)^2$$

$$+ K_{s1}(\alpha_2 \Sigma S_D)$$

$$Pb_T = \left(\frac{K_{so}}{\alpha_2 \Sigma S_D}\right) + K_{s11}\alpha_0\alpha_1(\Sigma S_D)^2$$

$$Zn_T = \left(\frac{K_{so}}{\alpha_2 \Sigma S_D}\right) + K_{s11}\alpha_0\alpha_1(\Sigma S_D)^2$$

where K_1 and K_2 are first and second ionization constants of H_2S

$$K_{so} = (M^{Z+})^{\frac{2}{Z}} (S^{-2})$$

$$K_{sn} \atop (n \neq 0) \quad = \quad \frac{\left[(M_{\frac{2}{z}}) (S^{-2}{}_{nH})\right]}{\left[S^{-2}\right]^n}$$

$$K_{s1n} \atop (n \neq 0) \quad = \quad \frac{\left[M(HS)^{-n}{}_{\frac{(n+2)Z}{2}}\right]}{\left[H_2S\right]\left[HS^-\right]^n}$$

$$K_{s0n} \quad = \quad \frac{\left[M_{\frac{2}{z}} S(HS)_n{}^{-n}\right]}{\left[HS^-\right]^n}$$

$$K_{sn0} \quad = \quad \frac{\left[M_{\frac{2}{z}} S(H_2S)_n\right]}{\left[H_2S\right]^n}$$

where M^{Z+} = trace metals

Z = valence

n = positive integer

Stability constants for these equations are as follows:

$$K_{s0}: \quad \frac{M_2S(s)}{Z} = \frac{2}{Z}M^{Z+} + S^{2-}$$

$$K_n: \quad M(HS)_{n-1}^{Z-(n-1)} + HS^- = M(HS)_n^{Z-n}$$

$$K_{sn}: \quad \frac{M_2S(s)}{Z} + nS^{-2} = \frac{M_2S_{n+1}^{-2}}{Z}$$

$$K_{s1n}: \quad \frac{M_2S(s)}{Z} + H_2S(aq) + nHS^- = \frac{2}{Z}M(HS)_{\frac{(n+2)Z}{2}}^{-n}$$
$$(n \neq 0)$$

$$K_{s0n}: \quad \frac{M_2S(s)}{Z} + nHS^- = \frac{M_2S(HS)_n^{-n}}{Z}$$

$$K_{sn0}: \quad \frac{M_2S(s)}{Z} + nH_2S(aq) = \frac{M_2S(H_2S)_n}{Z}$$
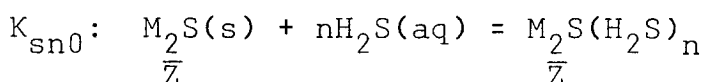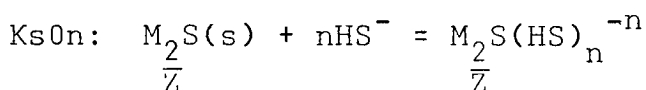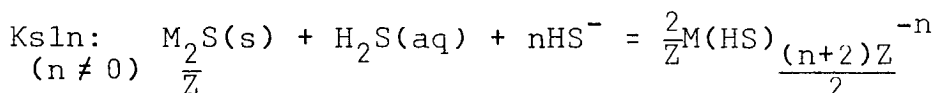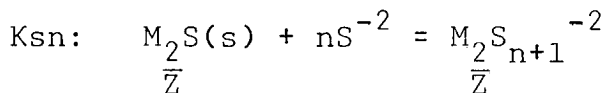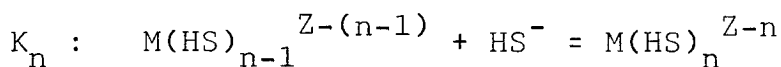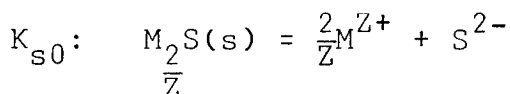
164. Under reducing conditions ($\Sigma S_D = 15 \sim 30$ mg/l, pH = 7 ~ 8), only the concentrations of cadmium and mercury were roughly close to the concentrations calculated by the above equations. The formation of sulfide complexes accounts for copper concentrations of roughly 10^{-5} ppb, which is much lower than the actual figure (0.02 ~ 0.55 ppb). The subsequent increase of copper in the interfacial water may be due to slow precipitation or nucleation, or may be due to the existence of organic and ammonia complexes.

165. The concentration of zinc calculated from the above equation can again only account for about 1/100 to 1/200 of the actual concentrations. Obviously, the formations of soluble carbonate, chloride, and organo-complexes account for most of the soluble zinc.

166. Information on nickel or lead sulfide complexes is lacking. However, it is unlikely that the sulfide com-

plexes account for the soluble concentrations observed. The spontaneous release of iron and manganese is obviously due to the existence of more soluble Fe(II) and Mn(II) compounds. It seems that FeS and MnS may be the most stable forms among inorganic ligands under sulfide-rich conditions. However, the results from calculations do not show such high solubilities. One possible reason may be that FeS and MnS colloids were so small that even 0.05 μm membrane filter could not capture them. The slow kinetics of precipitation or the presence of organo-complexes are two distinct possibilities.

Slightly oxidizing condition

167. In general, the concentrations of trace metals in interfacial seawaters under slightly oxidizing conditions were between the oxidizing and reducing conditions. Under oxygen-deficient conditions, due to the continued upward diffusion of dissolved sulfide from the sediment, the dissolved sulfide may overlap with the oxygen in the interface (as in silty clay sediment, where ΣS_D was approximately 0.05 mg/l). This dissolved sulfide may precipitate some of the dissolved trace metal species to metallic sulfides, and decrease the trace metal concentration in soluble phase.

Controlling Mechanisms for the Transport of Nutrients

Oxidizing condition

168. The results from Figures 14 - 16 show that under oxidizing conditions, organic nitrogen can be released to the 1 ppm range for silty and sandy types of sediment, and up to 10 mg/l in clayey-type sediment. This seems to correlate well with the total concentration of organic

nitrogen in sediment phase. Further hydrolytic reactions will lead to the formation of ammonia and reduction in the concentration of organic nitrogen. The existence of ammonia will stimulate the autotrophic activities as follows:

$$NH_3\text{-}N \xrightarrow{\text{Nitrosomonas}} NO_2\text{-}N \xrightarrow{\text{Nitrobacter}} NO_3\text{-}N$$
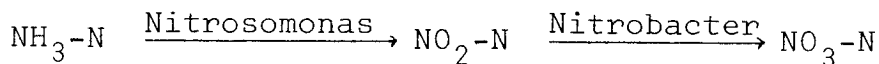
Apparently, the diffusion of organic nitrogen from interstitial water, hydrolytic action on complex organic compounds and sorption phenomena all contribute to the concentration of organic nitrogen in the interfacial waters.

169. The NH_3-N is continuously converted to NO_2-N through ecologically-mediated oxidation. However, NO_2-N is short-lived in a strongly oxidizing environment. It will finally be converted to the only stable form, NO_3-N, in oxidizing condition. Finally, NO_3-N also seemed to be decreased, probably as a result of biological uptake and ion exchange. For these reasons, it is suggested that biological activity is the major force in regulating the concentration of nitrogen compounds in the sediment-water interfaces.

170. For the P-compounds, total phosphate may come mainly from the diffusion of interstitial water and hydrolytic reactions on complex organic compounds. Hydrolytic action on organic phosphate and condensed phosphate will increase concentration of orthophosphate under oxidizing conditions.

171. Diffusion from interstitial water and dissolution from solid forms were the main driving forces for release of dissolved silica. Even after 5 months of contact, the equilibrium condition is apparently not reached.

Reducing condition

172. The release mechanism for dissolved silica in the reducing condition is the same as that for oxidizing conditions. However, under reducing conditions, $FePO_4$ solids will disappear, releasing $Fe(II)$ and PO_4^{-3}. The route for nitrogen compounds under reducing conditions is reversed from that of oxidizing conditions, and follows: $NO_3^- \rightarrow NO_2^- \rightarrow NH_3$ through biologically-mediated reduction. The organic nitrogen also converts to NH_3 through hydrolytic decomposition. NH_3 may also derive from diffusion of interstitial water. As a result, in the experiments, NH_3-N concentration was continuously increased while other dissolved nitrogen compounds were decreased.

Amount of trace metal transport

173. Under actual conditions, data on the amount of transport through interfaces are more useful. In general, the transport amount of most interfaces was found to be in the $\mu g/m^2$ range after 60 days of contact. Iron, manganese, zinc, and nickel may fall in the mg/m^2 range under some conditions (Figures 23 - 26). For example, under reducing conditions in silty sand sediment after 60 days of contact, iron may release to about 180 mg/m^2, and manganese may release to about 18 mg/m^2. In an oxidizing environment in silty sand sediment, after 60 days of contact, nickel may release to about 2.4 mg/m^2. Under a reducing environment, copper, mercury, and zinc may even deposit to the sediment. The amount of copper, mercury, and zinc scavenged under reducing conditions from overlying seawater by silty sand sediment is about 100 $\mu g/m^2$, 20 $\mu g/m^2$, and 60 $\mu g/m^2$, respectively; and for silty clay sediment, about 70 $\mu g/m^2$, 18 $\mu g/m^2$, and 70 $\mu g/m^2$, respectively. Selective data on the transport amounts of trace metals under different conditions are shown in Figures

23 - 26.

174.   From three parameters, (1) the transport amount,
(2) the overlying seawater conditions, and (3) the dilu-
tion factor of the overlying seawater, the pollution poten-
tial of the sediment may be estimated.   This information
is extremely useful in evaluating the long-term potential
water-quality effects of dredging activities.

<u>Changes of Geochemical Phases after</u>
<u>Long-Term Exposure to Different Redox Conditions</u>

<u>Changes in sediment characteristics</u>

175.   The general characteristics of the surface sedi-
ments were found to change after long-term exposure to
different overlying seawater conditions.   Under oxidizing
conditions, the surface sediment color gradually turned
to brown as the contact time was increased.   The color
changes penetrated nonhomogenously to about 2 cm from the
top of the sediment.   Under reducing conditions, the sur-
face sediment showed dark black color with a very light
yellow microfilm on the top.   This dark black color is
not much different from the original color of both silty
clay and sandy silt sediments, but is darker than the ori-
ginal color of the silty sand sediment.   Under slightly
oxidizing conditions, a light nonhomogenous brown color
was observed.

176.   The brown color, probably caused by the presence
of dissolved oxygen in the system, may result from iron
oxide and elemental sulfur.   The yellow microfilm observed
under reducing conditions probably came from organo-metal-
lic complexes as mentioned by Shapiro (121) and Ghassemi
and Christman (122).   The surface colors of the resettled
sediments were relatively close to those of similar redox

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conditions in the controlled tests.

177. The other main characteristics of the surface
sediments are listed in Table 41. It is apparent that in
the resettled sediments the concentrations of chemical
species on the surface were increased, but the dry weight
content was decreased. These phenomena are caused by the
accumulation of finer particles on the top layer without
compaction. For the tests with controlled redox condi-
tions, the organic fraction remained relatively unchanged.
Immediate oxygen demand and acid-soluble sulfide were
found to decrease drastically (Table 41) due to the pene-
tration of oxygen into the sediment.

Changes of geochemical fractions

178. The results of the sequential selective chemical
treatment of different types of sediment after long-term
incubation under different environmental conditions are
given in Tables 42 to 49 (listed percent of trace metal
partitioning) and in Figures 27 to 38 (given the concentra-
tion of trace metals in different geochemical phases). The
results of the partitioning of different fractions for
individual elements are discussed separately as follows.

Cadmium

179. The most significant finding for the analysis of
cadmium is the increase in the water soluble, exchangeable,
and carbonate fractions and the decrease in other fractions
under all types of overlying seawater conditions. Weber
and Posselt (123) suggested that in most environmental
circumstances the controlling solid of cadmium is hydrox-
ide or carbonate, and if

$$R_1 = \frac{(OH^-)^2}{(CO_3)^=} < 0.00423$$

the system will be controlled by $CdCO_3$. In this study, it was found that the R_1 values were smaller than 1×10^{-9} (Table 50). Therefore, the $CdCO_3$ would become the dominant species due to the abundance of the carbonate species in the interstitial water. It was also found that not only did the concentration of biogenic and nodular hydrogenous fractions decrease, but the residual fraction decreased as well (a decrease of 14% to about 3% for silty clay and 9% to 4 - 5% for silty sand sediment). This finding differs greatly from the traditional assumption that the lithogenic fraction is unreactive.

180. Under controlled redox conditions, cadmium concentrations were found to be higher under oxidizing conditions in the interstitial water phase (Figures 27-28). The same trend is also shown for cadmium in the interfacial water. The concentrations of the water soluble and exchangeable phases were at a very low level (Figures 29 - 32), but still showed that oxidizing conditions produced higher concentrations. For cadmium attached to the ferromanganese nodules, it seems that the oxidizing conditions showed less cadmium than did the reducing condition, probably due to the fact that under an oxidizing environment more oxide or hydroxide is converted to carbonate.

Chromium

181. Little is known about the geochemical phases of chromium in sediments. Morgan (124) proposed that in sewage the greatest amount (>90%) of Cr(III) will exist as solid $Cr(OH)_3(s)$, and that when the sewage is discharged to the ocean most of the Cr(VI) may also be reduced to $Cr(OH)_3$. In this study, about 30 - 50% of the total chromium is marine-derived; the rest, about 68% for silty clay to about 53% for silty sand sediment, is lattice-held. The results (Table 43) show that after about 4 to 5 months of

incubation the mineral residue fraction did not show any significant changes. For the authigenic fraction, both reducible phases were found to have no significant change. However, for the organic and sulfide phases, a slight decrease under oxidizing conditions was observed. Due to the decrease in the organic and sulfide phases, the amounts in exchangeable and acetic acid extractable phases were increased under oxidizing conditions (Table 43 and Figures 27 - 36). The concentration in the interstitial water was found to decrease under all redox conditions (Figures 27 - 28) and to decrease as the environment becomes more reducing. This is probably due to the increase in the hydroxide fraction.

Copper

182. Under an oxidizing environment, the amount of copper was found to increase in all phases of the non-nodular hydrogenous fraction and to slightly increase in the reducible fraction, while in the oxidizing environment the sulfide and organic fractions were slightly decreased. There was no marked change for the mineral residue fraction under different conditions after incubation (Table 44 and Figures 27 to 38). Under reducing conditions, the soluble and exchangeable phases were undetectable. These phenomena are quite reasonable because copper can be strongly adsorbed by clay minerals (125). Moreover, in a reducing environment, if there is any free copper ion present in soluble phase or exchangeable phase, then through the following reaction:

$$Cu^{+2} + MS \rightarrow M^{+2} + CuS \qquad (M = metals)$$
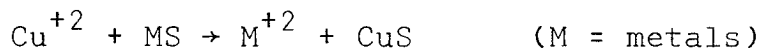
many other metallic sulfides can be replaced by Cu^{+2} to form very strong CuS solids (126).

183. Like chromium, under an oxidizing environment,

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the increase of copper in the water soluble, exchangeable, and carbonate fractions mainly results from the decrease of copper-organic and sulfide compounds. In this environment, the amount of increase of copper in the interstitial water was larger only than the increases for cadmium and chromium, but in the water soluble phase only the increase for manganese in silty clay sediment was larger, among the elements studied (Figures 27 - 30). This copper in interstitial water increased to 45 µg/kg and 75 µg/kg of dry sediment for silty clay and silty sand sediments, respectively (Figures 27 - 28). Under oxidizing conditions, the increase in copper in all phases of the non-nodular hydrogenous fraction (leachable by water, ammonia salts, and acetic acid) was very distinct. As mentioned by Krauskopf (125) and Garrels (127), this trend is probably due to the formation of carbonates and hydroxides, and by oxidation of organic and sulfide compounds.

184. In general, the increasing rate of the amount of acetic acid extractable and easily reducible phases is higher for clayey sediment than for sandy sediment, but the increasing rate of soluble and exchangeable phases is higher for sandy sediment than for clayey sediment. The latter finding differs from the results of Macias (128).

Iron

185. The transformation of geochemical phases and kinds of solids in different fractions of iron has been more thoroughly studied than for other trace metals. In general, the exchangeable phase of iron contains Fe^{+2} and $[Fe(OH)_n]^{(3-n)+}$ (129). The acetic acid extractable phase may contain oxyhydroxides (e.g., $Fe(OH)_3 \cdot nH_2O$ or geothite) or may also include a small amount of freshly precipitated FeS. As mentioned by Berner (130), some coarse-grained

iron minerals derived from land sources may contain Fe-silicate or other $FeCO_3$, Fe_2O_3 and Fe_3O_4. These iron sol-ids might not have a chance to react with sulfide in recent anaerobic marine sediments. Therefore, the acetic acid extractable phases may also include $FeCO_3$--which cannot be formed in the ocean. The iron oxide material can only slightly dissolve (usually 5%) in acetic acid even at a temperature of $100^{\circ}C$ (5). As mentioned previously, up to about 50% of the iron oxide minerals could be included in the easily reducible phase and about 90% of the total iron in the nodules could be extracted by the reagents of mod-erately reducible phase.

186. In this experiment, about 2/3 to 3/4 of the iron was of mineral-residue origin. Although the changes in iron in this residual phase were not obvious, a slight de-crease of iron under oxidizing conditions was still ob-served in silty sand sediment (Table 45). In a comparison between different conditions, high values of iron in the acetic acid extractable phase and reducible fraction were found under an oxidizing environment (Table 45 and Figures 33 - 34). The results also show that most of the acetic acid extractable phase and nodular fraction came from the biogenic fraction, and some might even have come from the residual fraction. Therefore, when dissolved oxygen is present, the oxyhydroxides and iron oxides may be increased in the sediment due to the oxidation of biogenic species or some weak lithogenic minerals.

187. The submerged soil in the reducing state which liberated large amounts of exchangeable iron has been re-ported (131,132). However, in this study, the exchangeable iron was surprisingly low under all redox conditions after incubation (< 6.5 x 10^{-6} ppm of dry sediment)(Table 45). This phenomenon was probably due to the fact that the sedi-

ments contain higher amounts of organic matter than do soils (133), and that iron has a great affinity for organic matter. Oloum, et al, (134), mentioned that the Fe-organic complexes in soil extracts were so strong that even EDTA or sodium-saturated cation exchanger could not replace the iron in the organic matter. It is quite possible that the exchangeable iron in the original sediment might gradually be changed to Fe-organic complexes either as solids or as soluble forms. The soluble forms are removed in the interstitial water phase, while the solid complexes are too strong to be exchanged by ammonium acetate in this experimental procedure. As a result, no exchangeable iron can be found in the long-term incubation of near-shore marine sediments.

188. The iron in the water soluble phase was also very low (Table 45). This is due to the solubility of controlling solids for iron with very small solubility products (reducing pK = 16.9 - 18.2, oxidizing pK = 37.3 - 43.3) (132,135). Double-distilled and deionized water could hardly increase the soluble iron.

189. There was no clear trend of change in iron concentration in the interstitial water under different redox conditions (Figures 27 - 28). When the dissolved oxygen level increased, the silty clay sediment showed an increase in iron in the interstitial water; conversely the silty sand sediment showed a decreasing trend. It is known that the increase of soluble iron in aqueous solution may be due to the chelation and/or peptization effects. Therefore it can be speculated that the complex formation (either from soluble form or from colloids) and those controlling solids (freshly precipitated FeS and greigite in the reducing state, and freshly precipitated ferric hydroxide in the oxidizing state) may compete against each other

in such a dynamic system. The ambiguous trend of the concentration of iron in the interstitial water may be simply the composite effects of the colloidal behavior, complexation, and solubility.

Manganese

190. The changes of manganese in different geochemical fractions seem to be quite complicated (Table 46 and Figures 27 - 38) and differ from the general trends of other trace metals. The trends in changes of manganese partitioning were different in the various types of sediment, even under the same redox conditions. With the same sediment at different redox conditions, the results for interstitial water, water soluble, exchangeable, and easily reducible phase are shown to be higher for the oxidizing, lower for the slightly oxidizing, and higher again for the reducing state (Table 46 and Figures 27 - 28 and 37 - 38). These results are probably caused by the existence of a great variety of manganese compounds. Mandal (131) suggested that the reducible manganese comprises higher oxides such as MnO, MnO_2, Mn_2O_3, and Mn_3O_4. Ponnamperuma (136) mentioned that more than 150 non-stoichiometric oxides of manganese ranging from $MnO_{1.2}$ to $MnO_{2.0}$ have been found in nature. The higher oxides may exist in different crystalline and amorphous states as well as in co-precipitates with iron and other oxides (136,137). Besides manganese oxides, solids like $MnCO_3$, manganite ($MnOOH$), braunite $[(Mn_2Si)_2O_3]$, and psilomelane $[BaMn(II)$ $Mn(IV)_8O_{16}(OH)_4]$ can exist under an oxidizing environment while $MnCO_3$ or probably MnS (not stable) may be present under a reducing environment (136-138). As for the soluble forms, Mn can exist as Mn^{+2}, stable bicarbonate complex ($MnHCO_3^+$), and neutral sulfate complex ($MnSO_4^O$), as

well as organic complex (134,136,139). Manganese may also
exist as colloidal dispersions (125), and these colloids
may be fine enough to pass through the filter (140). In
view of these complicated phenomena and the inadequacy of
reliable data on the chemistry or mineralogy of manganese,
the explanation of the geochemical phases of manganese is
a difficult task.

191. In general, manganese in the interstitial water
and water soluble phases was found to increase after incu-
bation, with the highest concentrations found under oxi-
dizing conditions. The manganese content in these two
phases decreased when the oxygen level decreased, but in
the interstitial water of silty sand sediment, manganese
increased again under extremely reducing conditions. In
the soluble phase of silty clay sediment, this increasing
trend is also shown under reducing conditions. The change
of the dissolved manganese in both phases under different
redox conditions may come from the change of solids and
the complex formation. The increase of manganese under
oxidizing conditions may be due mainly to the increase in
the solubility of solids because the oxidizing environment
favors the formation of $MnCO_3$ and other lower manganese
oxides from those anaerobic sediments. The increase of
manganese under reducing conditions may result mainly from
complex formation, because the reducing environment can
release more ligands (Table 50).

192. As mentioned by Jackson (129), the exchangeable
manganese can equilibrate with colloidal hydrated $MnO_{1\ to\ 2}$
and soluble Mn^{+2}. The increase of both the colloidal hy-
drated $MnO_{1\ to\ 2}$ or soluble manganese may increase the
exchangeable manganese, explaining why exchangeable man-
ganese follows the same trend as manganese either in the
interstitial water or in the acetic acid extractable phase

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(Table 46 and Figures 27 - 36).

193. The increase of the acetic acid extractable phase
under oxidizing conditions is evidence of the formation of
carbonate or some of the reactive oxides (136,141). The
biogenic fraction of manganese is relatively unreacted
compared to that of other trace metals (Table 46 and Fig-
ures 35 - 36), since not much difference was observed be-
tween the different redox conditions. Therefore, the in-
crease of nodular and non-nodular hydrogenous manganese
may come mainly from the mineral residue fraction. High
values of marine-derived manganese in the pelagic sedi-
ments (68 - 88%) had been reported by several researchers
(4,10,11). These high values are probably due to the
transformation of some of the lithogenic fraction to the
authigenic fraction after a long period of residence.

Nickel

194. The results of the nickel partitioning are given
in Table 47 and Figures 27 - 38. Due to the relatively low
concentration of nickel in the sediments and the low sen-
sitivity of nickel in atomic absorption determination, and
possibly to the low precision of the extraction method
used for this particular element, errors were very large
in the reducible phase (easily reducible phase, about 20%
deviation; moderately reducible phase, about 16% devia-
tion). Nevertheless, the trends of transformation for
nickel can still be discerned. Generally, the amount of
nickel in the interstitial water can be increased by ad-
ding oxygen to the overlying seawater (Figures 27 - 28).
The transformation trend for nickel in the soluble phase
is unclear (Table 47 and Figures 29 - 30). The results for
the exchangeable and acetic acid extractable phases were
similar; when the dissolved oxygen was increased in the
interfacial water the amounts of nickel in these two

phases were also increased. Organic sulfide phase was
also altered by dissolved oxygen, following the same trend
as the other trace metals. As for the reducible fractions,
there is no discernable trend (due to low precision), but
it seems that oxygen can slightly increase the amount of
nickel in this fraction.

195. Information on the geochemistry of nickel is
still lacking. The ion ratio method was applied here with
the data from Latimer (142):

$$R_1 = \frac{(OH^-)^2}{(CO_3^=)} = 1.18 \times 10^{-9}$$

$$R_2 = \frac{(S^=)}{(CO_3^=)} = 2.21 \times 10^{-14}$$

$$R_3 = \frac{(S^=)}{(OH^-)^2} = 1.88 \times 10^{-5}$$

$$R_4 = \frac{(SO_4^=)}{(CO_3^=)} = 2.57 \times 10^5$$

$$R_5 = \frac{(SO_4^=)}{(OH^-)^2} = 2.18 \times 10^{14}$$

196. From Table 50, it could be assumed that nickel
sulfide could be the solubility-controlling solid for re-
ducing conditions and that nickel hydroxide or carbonate
could be the controlling solid for oxidizing conditions.
In most cases the $NiCO_3$ seems more stable under oxidizing
conditions due to the increase in carbonate concentration.
This increasing trend of $NiCO_3$ under oxidizing conditions
can explain why the amount of acetic acid extractable
phase increases under oxidizing conditions. The solubili-
ty of Ni^{+2} was also increased when nickel was transferred
from NiS (in the original sediment) to $NiCO_3$. And due to

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the increase of Ni^{+2}, the concentration of nickel complexes also increased. This chain of increasing concentration was the main reason for the enrichment of nickel in the interstitial water and the exchangeable phase.

Lead

197. The results of lead partitioning in sediments are shown in Table 48 and Figures 27 - 38. There is no observable change in lead concentration in the lithogenic fraction; only sandy sediment showed a decrease when oxygen was increased. The nodular hydrogenous fraction of lead was found to increase slightly when dissolved oxygen was present, but the change in sandy sediment was negligible. The changes for the sulfide and organic fractions of lead were similar to those of other trace metals, with a negative relationship to dissolved oxygen (again the change for sandy sediment was unclear). In the acetic acid extractable phase, there is a trend of increase in lead for clayey sediment, a trend of decrease for sandy sediment, and no significant change for silty sediment when dissolved oxygen was increased.

198. No significant amount of lead in the exchangeable phase was found by the atomic absorption direct injection (HGA) method. The lead in soluble and interstitial water phases could be detected, and the concentration was also found to increase under aerobic conditions. However, the lead in soluble phase also seems to be increased in the reducing sediment. Leckie and James (126) and Garrels (127) suggested that the lead solids might exist as PbS, $PbCO_3$, $PbSO_4$, and $Pb_3(OH)_2(CO_3)_2$ in the sediments. From the ion ratio method:

$$R_1 = \frac{(OH^-)^2}{(CO_3^=)} = 2.80 \times 10^{-2}$$

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$$R_2 = \frac{(S^=)}{(CO_3^=)} = 4.21 \times 10^{-16}$$

$$R_3 = \frac{(S^=)}{(OH^-)^2} = 1.50 \times 10^{-14}$$

$$R_4 = \frac{(SO_4^=)}{(CO_3^=)} = 8.67 \times 10^4$$

$$R_5 = \frac{(SO_4^=)}{(OH^-)^2} = 3.10 \times 10^6$$

$$R_6 = \frac{(Cl^-)^2}{(CO_3^=)} = 1.07 \times 10^8$$

$$R_7 = \frac{(Cl^-)^2}{(OH^-)^2} = 3.81 \times 10^9$$

$$R_8 = \frac{(CO_3^=)}{[(OH^-)^2(CO_3^=)^2]^{1/3}} = 2.77 \times 10^{-7}$$

199. Comparing these R values to Table 50 indicates
that under aerobic conditions $PbCO_3$ is the solubility-
controlling solid, and PbS is the controlling solid when
hydrogen sulfide exists. Therefore, it is reasonable to
speculate that at the site of oxidation (i.e., at the sur-
face of the sediment particle under aerobic conditions)
the PbS was gradually oxidized by dissolved oxygen and
converted to $PbSO_4$, and the $PbSO_4$ gradually converted to
$PbCO_3$ on the outer zone of the particle. These transfor-
mations could produce more lead in the acetic acid extracta-
ble phase, so that the interstitial water and soluble pha-
ses were also increased. The amount of $PbCO_3$ derived from
the organic and sulfide phases were also increased. The
amount of $PbCO_3$ derived from the organic and sulfide phase
might be derived mainly from the sulfide phase instead of
the organic phase, due to the low rate of oxidation of

organic matter in sediment. This is also true for other trace metals. The changes in lead in the nodular hydrogenous fraction could be derived from either the biogenic fraction or from the decrease of ferro-manganese nodules.

Zinc

200. The results of the study of zinc are given in Table 11 and Figures 27 - 38. Like most trace metals, the geochemical fractions of zinc could be altered by dissolved oxygen and hydrogen sulfide after long-term incubation.

a. Interstitial water phase--zinc showed a positive relation to D.O. (i.e., concentration increased as D.O. increased) in sandy sediment, and a negative relation existed in clayey and silty sediment.

b. Water soluble phase--only a trace amount of zinc was found in sandy and silty sediments, but enrichment was found under both strong oxidizing and strong reducing environments for clayey sediment.

c. Exchangeable and acetic acid extractable phases-- zinc was increased after incubation under all conditions, with the highest concentration under oxidizing conditions.

d. Biogenic fraction--zinc showed a negative relation to D.O.

e. Nodular hydrogenous fraction--zinc was found to slightly decrease in the oxidizing environment in clayey sediment, but no significant change was found in sandy sediment.

f. Residual fraction--No significant trend was observed in this residual fraction.

201.   In order to explain the above phenomena, informa-
tion on zinc solids is necessary.   Zinc may be present as
oxide (ZnO), sulfide (ZnS), silicate (e.g., $Zn_4(OH)_2Si_2O_7$
$\cdot H_2O \cdot Zn_2SiO_4 \cdot nH_2O$), carbonate ($ZnCO_3$), and hydroxide
($Zn(OH)_2$) in the sediments (125-127).   In the reducing en-
vironment, the sulfide solid is the most stable form.   But
when oxygen is introduced into the system (as discussed in
the section on lead), the ZnS will change to other stable
forms.   From the ion ratio method (data from Ref. 142):

$$R_1 = \frac{(OH^-)^2}{(CO_3^=)} = 2.25 \times 10^{-7}$$

$$R_2 = \frac{(S^=)}{(CO_3^=)} = 8.00 \times 10^{-14}$$

$$R_3 = \frac{(S^=)}{(OH^-)} = 3.56 \times 10^{-7}$$

$$R_4 = \frac{(SO_4^=)}{(CO_3^=)} = 6.80 \times 10^{7}$$

and also from Table 50, $ZnCO_3$ may be shown as the solu-
bility-controlling solid under aerobic conditions in this
experiment.   This was also mentioned by Krauskopf (125)
and Garrels (127).   Lindsay (137), however, suggested that
the controlling solid of zinc for soil is an unknown com-
position of zinc solids--"Zn-soil."   Due to the complexity
of this experimental system, the real controlling solid is
usually unknown for dynamic conditions such as those of
soil, but the $ZnCO_3$ formation shows the trend of transfor-
mation.   This trend can be used to explain the changes in
zinc concentrations in the above-mentioned geochemical
phases.

202.   The variations in zinc concentration between
different types of sediment in the interstitial water are

not well known. The increase in zinc concentration under
oxidizing conditions in interstitial water in sandy sedi-
ment is probably due to solids of higher solubility plus
complex formation; but for clayey sediment, zinc enrich-
ment in the reducing interstitial water is probably due
to organic complexes. The same phenomena can also be used
to explain the water soluble phase.

Transformation of geochemical phases for the resettled test
without redox control

203. The total concentration of trace metals in the
sediment was increased to the surface after resuspension
of the sediment, caused by the redistribution of the sedi-
ment particles. The experimental data show that this in-
crease was larger in the sandy sediment than in the clay-
ey sediment. Within the same sediment, the increase in
the concentration of trace metals is not identical. The
order of increase and the increasing times are listed as
follows:

a. Clayey sediment: Cu (1.97) > Pb (1.84) > Zn (1.67)
> Cd (1.63) > Ni (1.25) > Cr (1.15) > Fe (1.09)
> Mn (1.06)

b. Sandy sediment: Cd (5.62) > Cu (3.37) > Pb (2.85)
> Zn (2.65) > Fe (2.55) > Ni (2.46) = Cr (2.46)
> Mn (1.29)

204. From the above order, we know that copper, lead,
cadmium, and zinc were more concentrated in the smaller
particles. And, surprisingly, these four elements also
had the lowest lithogenic fraction in the original sedi-
ments (only about 2 - 13% of the total; see Tables 42 - 49).
This means that most of the authigenic fraction is con-
centrated in the smaller particles and that trace metals

with a greater authigenic fraction can increase the trace
metals in the surface layer after the resuspension of sedi-
ment.

205. Conclusions drawn from this resettled test show
that, in general, resuspension causes the increase of bio-
genic, reducible, acetic acid extractable, or, probably,
exchangeable trace metals, compared to the non-resettled
test. And after long-term contacting with aerobic sea-
water, these biogenic and reducible forms of trace metals
were transferred to acetic acid extractable and exchange-
able forms; as a result, the pollution potential was in-
creased. But this pollution potential may be caused not
only by the increase of the solubility of the solids, but
may also result from the types of ligands (e.g., reducing
conditions produce fewer high solubility solids but more
organic ligands in the seawater). Therefore, the over-
lying seawater condition is the real dominant factor for
controlling the direction of transport of trace metals.
In the field situation, the overlying seawater conditions
may be influenced both from inside (caused by the oxida-
tion of organic matter) or outside (caused by current).
Only in the case of stagnant bottom seawater and sediment
with high organic contents is it possible that the direc-
tion of transport of trace metals could be dominated by
the sediment itself.

Associations of Organic Substances with Trace Contaminants

Trace metals

206. Sediments used for studying interactions of
trace contaminants with organic substances were collected
from the stations shown in Figure 1. However, the charac-
teristics of these sediments differ greatly from those of

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other studies cited in this report. Sediments for the organic study were collected shortly after a prolonged storm period. Trace metal analyses were performed for silver, aluminum, arsenic, cadmium, chromium, copper, iron, manganese, nickel, lead, vanadium, and zinc. The results are shown in Tables 51 through 57. A total of seven sediments were studied. The characteristics of the sediments may be different from those previously presented due to the storm.

207. Concentrations of aluminum and iron are found to be the highest in total organic content (NaOH-extracted) and in the humic and fulvic acid fractions of all sediments. The percentage of total aluminum and iron associated with the total organic content (NaOH-extracted) varies from 0.69 - 3.49% for aluminum and 1.22 - 2.3% for iron. Silver and cadmium, on the other hand, were found to be in the lowest concentrations in all sediments, in both the NaOH-extracted total organic content and the humic and fulvic acid fraction. The percentages of total silver and cadmium associated with total organic content (NaOH-extracted) varies from 0.71 to 11.1% for silver and 0.89 to 4.7% for cadmium. Manganese associated with NaOH-extracted total organic content and humic and fulvic acid is shown to be insignificant in terms of total trace metal concentration in all samples.

208. The high concentration of aluminum associated with the NaOH-extracted organic matter and humic and fulvic acid is probably due to the presence of finely-dispersed clayey particles (<0.1 μm) which were brought into solution during the extraction process. Among all trace metals studied, only six elements (arsenic, cadmium, nickel, lead, vanadium, and zinc) show any significant association with the organic phases.

209. It is very difficult to correlate trace metal concentration in organic phases to the sediment characteristics. Similarly, it is somewhat difficult to directly correlate total organic content to the trace metal concentration in the organic phases even though these two parameters are usually mentioned together. In all probability, NaOH extraction of organic substances is not complete, especially in sediment with a large surface area. This is evident in Table 5. It is noted that the ratio of $TO(NaOH)_{sx}/TOC_{sed}$ is highest with stations 3 and 4, both silty sand stations. In the silt or clay sediment types with a large surface area, the complete extraction of organic matter containing humic and fulvic acid may take months. However, for practical purposes, the procedures used are deemed to be sufficient.

210. In light of the general, non-specific nature of the extraction and separation of humic and fulvic acid, the exact quantities of trace metals complexes with humic and fulvic acids are difficult to assess. Due to the "harsh" extraction treatment, initially high pH and separation with 3N HCl at low pH, the very strong bond energies that exist between trace metals and especially humic acid is implied. The extraction essentially involves the physical separation of the organo-metallic complex. Since wet sediment was used in the alkalimetric extraction (containing NaCl in pore water), it was necessary to use the deuterium arc background corrector for metal determination in all the organic phases.

211. Summarizing the data presented in Tables 51 to 57, significant fractions of trace metals such as silver, arsenic, cadmium, chromium, copper, nickel, lead, vanadium, and zinc are associated with organic fractions obtained through successive extractions with NaOH. More

abundant elements such as aluminum, iron, and manganese show no significant association. The importance of organometallic interactions is illustrated by the fact that the content of total organic carbon represents only 0.3 - 0.8% of sediment weight (Table 58) for Stations 1 to 6, and 1.7% for Station 7. However, most of the metal species associated with organic fractions through successive NaOH extractions are in the range of 3 - 10%. This represents an average concentration factor of 2 to 15 times in the organic fractions in comparison with the total sediment fraction. Since the possibility of biological uptake of these compounds exists, further study may be necessary.

Chlorinated hydrocarbons

212. During the early phases of this study, efforts were made to determine the presence of the soluble fraction of chlorinated hydrocarbons in interstitial waters, water columns, and sediment-water interfaces. These were made either by ultracentrifugation or filtration. Under no circumstances was a soluble fraction of chlorinated hydrocarbons ever detected. For this reason, later efforts were devoted to the study of chlorinated hydrocarbons in particulate phases.

213. The major effort in evaluating the effects of chlorinated hydrocarbons on water quality from the disposal of dredged sediments centered around three areas: (1) identification of the form of chlorinated hydrocarbons in sediment phase, (2) correlation of the particle size of sediment fractions with the concentrations of chlorinated hydrocarbons, and (3) relationship of the contents of macromolecular organic compounds to the concentration of chlorinated hydrocarbons. These will help to pinpoint the possible effects on the uptake of chlorinated hydrocarbons by the filter-feeding organisms and certain species of algae.

214. Another batch of sediments, from Stations 1 - 7, was again extracted with NaOH. In this batch only 11 - 68% of the TOC in sediments can be accounted for (Table 59), mostly in the range of 25 - 35%. This indicates that the remaining fractions, refractory organics, and lipids are still the predominant source of organic carbon in sediment. The use of 0.1N NaOH was found to contribute to the process of dehalogenation of some chlorinated hydrocarbons. Therefore, a homogenized sediment was split into two fractions. Humic and fulvic acids were extracted and analyzed for TOC. Another fraction of sediment was extracted for chlorinated hydrocarbons. Sediment particles of 8 μm or less were fractionated into 4, 2, 1, and 0.5 μm size fractions. At the same time, the sediment was again analyzed for TOC as well as for chlorinated hydrocarbons. The results are shown in Figures 39-43.

215. Results from the study of chlorinated hydrocarbons are shown in Table 60. The data shows that p,p'DDE constitutes 61 - 71% of the total DDT (t-DDT = DDE + DDD + DDT). Other isomers contribute to t-DDT as follows: o,p'DDE, 6.1 - 9.1%; p,p'DDD, 10.0 - 16.6%; o,p'DDD, 3.4 - 7.8%; p,p'DDT, 2.8 - 7.7%; and o,p'DDT, 2.6 - 4.6%. The results are quite similar to those of the latest works reported (65, 143). Dieldrin constitutes less than 1% of the total chlorinated hydrocarbons (t-DDT + Dieldrin + PCB's). For Stations 6 and 7, which are located in the proximity of a sewer outfall, the percentage of PCB's is very high, 45 - 65% of the total chlorinated hydrocarbons. For the rest of the stations, t-DDT and PCB's (mostly PCB-1254) constitute 87 - 92% and 8 - 19% of the total chlorinated hydrocarbons, respectively.

216. It has been suggested that about 1/3 of the humus can be removed from soil by extracting with alkali

(144). On the other hand, Schnitzer and Khan (145) claimed that the dilute aqueous NaOH solution is quantitatively the most effective reagent for extracting humic substances from sediments or soils. In this study, humic substances from sediments were extracted successively with 0.1N NaOH until the supernatant became virtually colorless; however, the actual amount of humic substance present in the sediment is still unknown. So it seems appropriate that $TOC(NaOH)_{sx}$, TOC_{HA}, and TOC_{FA} data listed in Table 59 are not to be considered absolute quantities. The relations of total organic carbon content of each fraction as well as total sediment and particle sizes of 8 μm or less are shown in Figures 39 to 41. This is similar to the results reported by Leland, et al. (146), that the amount of organic material in surficial sediments was directly proportional to the clay-size fraction (less than 2 μm) of sediment.

217. Figures 42 and 43 show that the concentrations of both t-DDT and t-chlorinated hydrocarbons increase with increasing contents of total organic carbon in the sediment samples. This is similar to the results taken from Southern Lake Michigan on the accumulation of t-DDT in lake sediment (146). O'Connor and Anderson (147) recently reported that the organic matter was an important contributor to 2,4,5-T adsorption, and in some soils might be the only adsorbent of significance. They also stated that the amount of the herbicide adsorbed per gram of organic matter was not constant, but adsorption tended to increase with organic matter. However, as shown in Figures 42 and 43, the t-DDT and t-chlorinated hydrocarbons are approximately proportional to $TOC(NaOH)_{sx}$, TOC_{HA}, and TOC_{FA} with relatively little data scattering. This may be an indication of the significance of humic substances for the adsorption

of chlorinated hydrocarbons. These results are reasonable
in view of the other studies (148,149).

218. Khan (62) investigated the adsorption of 2,4-D
from aqueous solution by a fulvic acid-clay complex and
proposed a physical type of adsorption. Ballard (59)
reported that in DDT-spiked humic extracts (HA+FA), 91%
of the added o,p'DDT was recovered in humic acids and the
other 9% in fulvic acids plus water, indicating that humic
acids are much more capable of adsorbing DDT than fulvic
acids. Although this implies that fulvic acids are much
less capable of adsorbing pesticides than humic acids, it
is still obvious that both are potential adsorbents. Nu-
merous workers (25,62,148 - 150) have reported the direct
relationship of the contents of organic matter and clay-
size particles. Since concentrations of chlorinated hy-
drocarbons are related to organic matter, particularly to
humic substances, a strong relation between very fine
grain size in sediments and chlorinated hydrocarbons is
also implied.

219. From the results of this study, it may be sug-
gested that the fraction of very fine silts and clays
(< 8 μm) and the amount of both humic and fulvic acids are
important factors in controlling the adsorption capacity
of chlorinated hydrocarbons in marine sediments. It is
reasonable to conclude from the data presented that chlor-
inated hydrocarbons will not be released to solution in
detectable quantity under normal conditions. However,
there is some conclusive evidence about their existence in
theparticulate phase. The association of chlorinated hy-
drocarbons with macromolecular organic substances such as
humic and fulvic acids may cause some uptake by marine
organisms upon resuspension of sediment. This is especial-
ly true in a confined area where dilution or current cir-

culation is limited.

220. From the data presented so far, it is obvious
that the release of trace metals from dispersion, settling,
and resedimentation of sediments are generally in the ppb
or sub-ppb range, both short and long term. These concen-
trations are well below the proposed numerical criteria for
ocean water established by Federal and State regulatory
agencies (152,153). Concentrations of soluble iron and
manganese, which are non-toxic, may range up to several
hundred parts per billion under anaerobic conditions;
however, in an oxidizing environment, these concentrations
are greatly reduced.

221. Due to the extremely low levels of metal concen-
trations in most seawaters, the relative factors of re-
lease in comparison with seawater backgrounds are very
misleading. For example, a ten-fold increase in the solu-
ble fraction of lead in most seawater will result in a
concentration ranging from 0.3 to 1.0 ppb, which is insig-
nificant even from the standpoint of the most restrictive
water-quality standards. The release of other metal spe-
cies can be described in the same manner.

222. Most of the nutrients are released in the sub-
ppm to ppm range, which would create little problem in
open-water disposal. The only potential problem is the
release of ammonia under anaerobic conditions in a con-
fined area with very little dilution from overlying water.
Under these conditions, ammonia concentration may increase
to over 10 ppm, which would create some physiological
problems for more delicate organisms. However, with some
circulation, this type of problem should disappear.

223. Both the column settling and long-term sediment-
water interfacial studies were run as a simulation of

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dredging conditions. A major deficiency of this type of
laboratory study is that dilution which could occur at
an open-water site cannot be properly reflected in the
laboratory setup. It should be realized that such a dilu-
tion is extremely difficult and perhaps impossible to
model under laboratory conditions. The measured concentra-
tions therefore represent the maximum conditions, and ac-
tual concentrations should be substantially lower than
those from laboratory measurements.

224. The only uncertainty of this study regarding the
water-quality impact of the open-water disposal of dredged
sediment is the association of trace contaminants with
suspended particulates. Even though there is no direct
evidence of adverse ecological impact from such opera-
tions, the potential of increasing uptake of contaminants
by filter-feeding organisms and certain species of algae
cannot be minimized. One possible solution to minimize
this problem is the direct treatment of sediment-water
mixtures by the addition of flocculants to improve the set-
tling characteristics of suspended particulates (154,155).

PART V: SUMMARY AND CONCLUSIONS

225.   This study encompasses most aspects of physico-
chemical effects of dredging operations on water quality.
The results show that concerns regarding the release of
any significant quantity of toxic materials into solution
phase during dredging operations and disposal are mostly
unfounded.   While some trace metals are released in the
parts-per-billion range, others show essentially no re-
lease pattern, with the exceptions of iron and manganese.
Most of the concentrations in soluble phase are well below
the recent proposed numerical criteria for ocean waters
(152,153).   Due to the extremely low concentrations of
trace metals in seawater, the relative factors of release
over the background levels should not be used as dredging
criteria.   Instead, appropriate numerical values based on
bioassay study should be used.

226.   The release of trace metals in soluble phase is
deemed to be ecologically insignificant.   However, trace
metals associated with certain fractions of organic phase,
such as humic and fulvic acids, are found to contain metal
species 2 to 15 times higher than the concentrations in
total sediment digests on a weight/weight basis.   The
availability of these organic compounds as a food source
for filter-feeders and algae may present some potential
problems.

227.   During the entire study, no soluble form of
chlorinated hydrocarbons has ever been observed.   Most of
the chlorinated hydrocarbons are found to be associated
with fine particles and macromolecular organic compounds.

This, together with trace metals associated with suspended particulates, may present some unknown effects after the disposal of dredged materials.

228. The releases of nutrients are found to be in the sub-ppm to ppm ranges, which may increase the productivity of open waters. In a confined area with little circulation and dilution, ammonia can be released to over 10 ppm under prolonged contact of sediment with anaerobic overlying waters.

229. With the exception of metal contents in interstitial waters, there is little correlation from the data obtained from geochemical fractionation, including gross sediment analysis, to the level of metal release found in both long-term and short-term experiments. The redox conditions of the overlying waters are the controlling factors for the release of metals.

230. Additional findings are summarized as follows:

1. The selective extraction procedures presented can be used successfully in determining different geochemical fractions with less than 10% deviation of mass balance for most trace metals.

2. The fraction of trace metals from land sources pollution and marine derivation is found to increase with decreasing sand content.

3. The ion exchangeable fractions of trace metals in these sediments follows the order:
   Fe > Mn > Zn > Ni > Cr > Pb > Cd = Cu

4. The percentage of cadmium, lead, and zinc in organic and sulfide extracts showed a strong relationship with sulfide concentrations and indicates that they are less mobilized in an anaerobic condition.

5. The lithogenous character of the trace elements decreases in the order:
   Cu > Mn > Fe > Cr > Ni > Pb > Zn > Cd

6. In column settling studies, iron, manganese, and nickel showed the highest degree of increase in soluble metal content; higher levels of increase were observed in oxygen-deficient environments.

7. Chromium, copper, lead, and zinc exhibited moderate release (<15 times seawater concentration), while silver, cadmium, and mercury showed very little change under all test conditions. The concentration of chromium remained steady under either reducing or oxidizing conditions.

8. The dissolved oxygen content and redox conditions to a large extent control the amount and species of soluble metal ions and nutrients. Immediate oxygen demand of most polluted sediments will present problems for disposal in a confined area.

9. In the long-term study, the organic-rich, sulfide-rich type of sediment with a high clay and silt content showed a comparatively low soluble trace metal concentraction and a higher nutrient release.

10. After sediments are resettled, the experimental data show that the nature of sediment, i.e. clay, silt, or sand, does not control the direction of metal transport. It is regulated mainly by the chemistry of the immediately overlying water as well as that of the interstitial water. The redox chemistry is the principal factor. In general, the concentrations of trace metals in the interfacial water were found to be in the sub-ppb to ppb ranges.

11. Under oxidizing conditions, with the exception of silver, chromium, and mercury, all other observed trace metals were found to be released in the sediment-water interface. In comparison with background seawater, cadmium, manganese, nickel, and zinc were significantly released, with copper, iron, manganese, and lead only moderately released. It is suggested that the release effect is mainly the result of carbonate, chloride, and organo-complexes formation.

12. Under oxidizing conditions, the nitrogen and phosphorus compounds increased during the beginning contact period (about 1 - 2 months) followed by a general decrease. NH_3 decreased to zero due to oxidation to NO_3^-. The concentration of silica was found to be steadily increased. The clayey-type of sediment was found to release more nutrients. Diffusion, bio-oxidation, desorption, and dissolution are the main regulatory mechanisms.

13. Under reducing conditions, iron and manganese were released to a very high level, almost to the ppm range. The concentrations of other trace metals were decreased to extremely low values in the initial contact period. As time passed, the concentrations of cadmium, copper, mercury, nickel, lead, and zinc were again increased. The deposition effect is a result of metallic sulfide formation. The redissolution effect is due to desorption from iron and manganese or clay minerals and the slow kinetics of the metal-sulfide precipitation, the formation of sulfide complexes, or the formation of organo-metallic complexes.

14. Under reducing conditions, the release phenomena for phosphorus and silicon compounds were the same as those in the oxidizing condition, but generally with

higher release rates as a result of lower pH under reducing conditions.

15. Under slightly oxidizing conditions, the concentrations of trace metals and nutrients were between those of the oxidizing and reducing environments.

16. The flux of metal transport across a sediment-water interface is primarily governed by the type of sediment and the overlying seawater conditions and the chemistry of the individual elements.

17. No significant difference was found between the resettled and non-resettled tests. The releasing pattern of trace metals and nutrients in the resettled tests was close to that obtained under similar redox conditions in the non-resettled tests. Therefore, the transport phenomena are controlled by the redox condition rather than by the physical characteristics of the sediment.

18. The release of metals transport in sediment-water interfaces is independent of the gross concentration of sediments. However, sediments with higher amounts of nutrients may release higher concentrations of nitrogen compounds.

19. Three to ten percent of trace metals such as silver, arsenic, cadmium, chromium, copper, nickel, lead, vanadium, and zinc are associated with organic fractions. obtained through successive extractions with NaOH. On a weight basis, this fraction generally contains 2 - 15 times higher concentrations of trace metals than the total sediments.

20. After long-term incubation, the characteristics of the surface sediment could be altered. In contacting with aerobic seawater, the IOD and acid-soluble sulfide

were gradually decreased and sediment color turned to brown. Either oxygen or sulfide could penetrate through the sediment-seawater interface.

21. The lithogenic fraction of some trace metals could be changed after four months of exposure to different environmental conditions. Under oxidizing conditions, the lithogenic fractions of manganese and nickel were gradually decreased and were converted to the authigenic fraction. Lead and iron showed only a slight decrease under oxidizing conditions in sandy sediment. The changes of this fraction for chromium, copper, and zinc were unclear.

22. Under oxidizing conditions, the easily and moderately reducible fractions of copper, iron, nickel, lead, and probably zinc and manganese were increased, but cadmium was decreased in this fraction.

23. All biogenic fractions were found to be decreased by oxidation. Copper and zinc had the highest percentage of decrease. Changes in manganese in clayey sediment and in iron in sandy sediment were unclear.

24. Phases in the non-nodular fraction could be increased by an increase in higher solubility solids under oxidizing conditions. In an oxidizing state, sulfide, silicate, or even oxide solids may be changed to carbonates, hydroxides, or relatively reactive oxides.

25. The concentration of cadmium, chromium, copper, manganese, nickel, and lead in all types of sediment, and of iron in clayey sediment and zinc in sandy sediment, were higher in the interstitial water under oxidizing conditions. In general, with the exceptions of iron, manganese, and zinc, this trend was similar to that in interfacial water.

26. p,p'DDE generally accounts for 60 - 70% of the total chlorinated hydrocarbons in the sediment, while PCB's (mostly PCB-1254) constitute almost 10 - 20% of the total. Other isomers of DDT and dieldrin account for the remaining fraction.

27. Concentrations of chlorinated hydrocarbons are closely related to the organic contents and particles of 8 μm or less in size.

231. The results show that concerns regarding the release of a significant quantity of toxic materials into solution during dredging operations and disposal are unfounded. The data from this study indicate that while some trace metals may be released in the ppb range, others show essentially no release pattern. Most of the concentrations in soluble phase are well below the allowable concentration levels of the ocean water discharge standards. However, the trace metals and chlorinated hydrocarbons associated with macromolecular organics and suspended particles released into the water column as a result of dredging activities may present some unknown effect. It is believed that the discrepancy between some field studies which show the release of trace contaminants and this study which shows very little release may result from the influence of suspended particulates on the concentrations of contaminants. Additional study should be focused on the chemistry of contaminants in the particulate phase and on mitigation processes.

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Table 5

Moisture Content and Particle Size Distribution of Sediments
from Sampling Stations* in Los Angeles Harbor

Parameter	Silty Sand Sta.#1	Sandy Silt Sta.#2	Silty Sand Sta.#3	Silty Sand Sta.#4	Silty Sand Sta.#5	Silty Clay Sta.#6
Moisture Content, %	30.5	43.5	31.0	26.0	29.2	43.0
Sand, % > 50 μm	77.0	48.5	71.0	80.0	71.0	12.0
Silt, % 50 – 5 μm	12.3	31.5	17.5	8.0	18.0	56.0
Clay, % < 5 μm	10.7	20.0	11.5	12.0	11.0	32.0

* Stations shown in Figure 1

Table 6

Characteristics of Sediments from Sampling Stations*
in Los Angeles Harbor

(units in ppm unless specified)

Parameters	Silty Sand Sta. #1	Sandy Silt Sta. #2	Silty Sand Sta. #3	Silty Sand Sta. #4	Silty Sand Sta. #5	Silty Clay Sta. #6
TOC**	1.09	1.90	2.0	0.84	1.11	2.12
COD	--	52,590	29,210	21,450	22,870	116,800
IOD	--	538	383	350	181	1,570
TVS**	--	4.59	2.80	1.97	2.10	10.1
$S^=$	--	258	163	102	269	1,670
Organic Nitrogen	--	357	689	588	459	2,820
Total Nitrogen	--	357	706	636	493	2,920
Total Phosphorus	--	886	679	644	787	1,470
Ag	4.48	16.9	7.1	3.5	5.4	10.2
Cd	2.42	1.90	0.66	0.66	2.45	2.20
Cr	89	175	94	67	77	178
Cu	45.2	119	51.0	35.0	47.5	568
Fe	31,610	40,830	28,980	28,560	33,520	45.180
Hg	--	0.685	0.28	0.27	0.33	1.43
Mn	502	429	422	381	487	493
Ni	21.6	35.3	23.0	18.2	21.9	47.2
Pb	39.2	67	47	32	35.6	332
Zn	115	205	106	94	112	612

--Not determined

* Stations shown in Figure 1

** In percent

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Table 7

Total Heavy Metal Content of Sediments
from Sampling Stations** in Los Angeles Harbor

(mg/kg dry weight)

Element	Sandy Silt Sta. #2	Silty Sand Sta. #3	Silty Sand Sta. #4	Silty Clay Sta. #6
Cd	1.9 ± 0.07	0.7 ± 0.01	0.7 ± 0.03	2.2 ± 0.2
Cr	175 ± 2.0	94 ± 3.5	67 ± 1.2	178 ± 1.0
Cu	119 ± 1.5	51 ± 1.7	35 ± 0.4	568 ± 103
Fe	40,830 ± 860	29,980 ± 1,044	28,560 ± 1,500	45,180 ± 680
Mn	429 ± 5	422 ± 11	381 ± 13	493 ± 9.5
Ni	35.3 ± 1.2	23.3 ± 1.0	18.2 ± 0.5	47.2 ± 2.0
Pb	67 ± 6.6	47 ± 4	32 ± 0.8	332 ± 26
Zn	205 ± 3.6	106 ± 4	94 ± 1.4	612 ± 112

* Average of three replicate analyses performed for each sediment
** Stations shown in Figure 1

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Table 8

Interstitial Water Analysis for Trace Metals*
of Sediments from Sampling Stations** in Los Angeles Harbor

Element	Sandy Silty Sta. #2	Silty Sand Sta. #3	Silty Sand Sta. #4	Silty Sand Sta. #5	Silty Clay Sta. #6
Cd	0.2	0.3	0.1	0.25	0.5
Cr	0.9	0.9	0.8	0.4	0.7
Cu	0.4	1.3	0.9	1.3	0.4
Fe	980	985	360	2,000	120
Mn	74	92	100	75	6.0
Ni	1.3	2.5	1.3	1.8	0.6
Pb	0.4	0.3	0.4	4.5	0.45
Zn	19	21	21	24	10

* In µg/l

** Stations shown in Figure 1

Table 9
Trace Metal Concentration[*] among Different Geochemical Fractions of
Sandy Silt Sediment (Sta. #2), Los Angeles Harbor
(mg/kg dry weight)

Treatment number	Extractant	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	Double-distilled water	0.0	0.01	0.0	0.0	0.0	0.01	0.007	0.06
2	1.0M ammonium acetate	0.0	0.02	0.0	39.5	1.16	0.04	0.0	0.01
3	1.0M acetic acid	0.16	11.4	0.05	3,919	49	2.6	7.2	44
4	0.1M hydroxylamine hydrochloride	0.90	3.7	4.2	683	9.3	0.9	17.0	32
5a	1.0M ammonium acetate + hydrogen peroxide	0.51	5.0	1.4	918	13.0	3.7	5.0	34
5b	0.01M nitric acid + hydrogen peroxide	0.50	4.8	1.4	821	9.9	3.8	1.2	30
6a	Sodium dithionite -citrate	0.0	29	3.2	3,885	6.8	3.4	0.25	9.0
6b	0.04M hydroxylamine hydrochloride in 25% acetic acid (100°C)	0.4	48	7.2	4,502	53	8.4	21.0	37
7a	Residual	0.31	117	96	31,700	395	30.0	31	99
7b	Residual	0.05	107	99	32,650	359	27.0	24	84
8a	Sum (1+2+3+4 +5a+6a+7a)	1.88	166	105	41,140	473	40.6	60	218
8b	Sum (1+2+3+4 +5b+6b+7b)	2.01	175	112	46,210	480	42.7	70	227
9	Gross concentration	1.90	175	119	40,830	429	35.3	67	205

[*]Average of two replicate analyses

Table 10

Trace Metal Concentration* among Different Geochemical Fractions of
Silty Clay Sediment (Sta. #6), Los Angeles Harbor
(mg/kg dry weight)

Treatment Number	Extractant	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	Double distilled water	0.0	0.011	0.0	0.0	0.0	0.01	0.008	0.06
2	1.0M ammonium acetate	0.0	0.008	0.0	66	2.0	0.007	0.0	0.009
3	1.0M acetic acid	0.07	5.3	0.04	5,060	37	3.0	1.0	50
4	0.1M hydroxylamine hydrochloride	0.23	4.0	0.09	889	9.0	1.0	20.0	122
5a	1.0M ammonium acetate + hydrogen peroxide	0.74	4.1	4.0	720	11.0	4.0	42	181
5b	0.01M nitric acid + hydrogen peroxide	0.62	2.5	2.5	639	8.6	3.8	11.0	159
6a	Sodium dithionite -citrate	0.0	19.0	1.1	2,545	7.0	2.1	0.4	28.0
6b	0.04M hydroxylamine hydrochloride in 25% acetic acid (100°C)	0.78	63	8.8	3,667	48	7.7	145	155
7a	Residual	0.82	157	1,000	28,580	367	28.0	223	210
7b	Residual	0.28	113	869	30,220	350	26.0	165	145
8a	Sum (1+2+3+4 +5a+6a+7a)	1.86	190	1,005	37,860	433	38.1		591
8b	Sum (1+2+3+4 +5b+6b+7b)	1.98	183	880	40,540	455	41.5	342	631
9	Gross concentration	2.2	178	568	45,180	493	47.2	332	612

*Average of two replicate analyses

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Table 11

Trace Metal Concentration* among Different Geochemical Fractions of Silty Sand Sediment (Sta. #3), Los Angeles Harbor (mg/kg dry weight)

Treatment Number	Extractant	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	Double-distilled water	0.0	0.005	0.0	0.0	0.0	0.01	0.006	0.05
2	1.0M ammonium acetate	0.0	0.006	0.0	37.0	1.5	0.03	0.0	0.16
3	1.0M acetic acid	0.35	4.0	2.4	1,796	34	1.5	6.8	30
4	0.1M hydroxylamine hydrochloride	0.16	2.0	3.5	510	6.3	0.4	8.0	12.0
5a	1.0M ammonium acetate + hydrogen peroxide	0.13	3.0	1.0	659	8.6	1.7	2.0	12.0
5b	0.01M nitric acid + hydrogen peroxide	0.12	2.8	1.1	579	6.6	1.8	0.5	10.0
6a	Sodium dithionite -citrate	0.0	12.0	1.6	2,528	5.6	2.2	0.1	4.0
6b	0.04M hydroxylamine hydrochloride in 25% acetic acid (100°C)	0.12	22.0	3.5	3,211	39	4.6	9.1	20.0
7a	Residual	0.12	65	34	21,900	354	16.5	22.0	59
7b	Residual	0.07	66	39	24,630	351	15.5	17.0	53
8a	Sum (1+2+3+4 +5a+6a+7a)	0.76	86	42	27,430	410	22.3	39	117
8b	Sum (1+2+3+4 +5b+6b+7b)	0.82	97	49	30,760	438	23.7	41	125
9	Gross concentration	2.2	178	568	45,180	493	47.2	332	612

* Average of two replicate analyses.

Table 12

Trace Metal Concentration* among Different Geochemical Fractions of Silty Sand Sediment (Sta. #4), Los Angeles Harbor (mg/kg dry weight)

Treatment number	Extractant	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	Double-distilled water	0.0	0.004	0.0	0.0	0.0	0.007	0.005	0.03
2	1.0M ammonium acetate	0.0	0.002	0.0	1.8	1.4	0.02	0.01	0.11
3	1.0M acetic acid	0.35	2.2	5.0	975	24	1.0	5.4	30
4	0.1M hydroxylamine hydrochloride	0.08	1.4	530	5.4	0.25	6.0	6.0	7.7
5a	1.0M ammonium acetate + hydrogen peroxide	0.07	1.7	1.0	567	7.4	1.6	1.8	8.0
5b	0.01M nitric acid + hydrogen peroxide	0.06	1.7	1.0	536	5.5	1.6	0.54	6.0
6a	Sodium dithionite -citrate	0.0	6.8	1.1	2,124	3.7	1.6	0.0	2.7
6b	0.04M hydroxylamine hydrochloride in 25% acetic acid (100°C)	0.08	13.0	2.6	2,924	36	4.9	8.3	16.0
7a	Residual	0.06	52	20	17,940	355	13.6	16.5	49
7b	Residual	0.03	51	24	22,100	356	13.0	14.0	43
8a	Sum(1+2+3+4 +5a+6a+7a)	0.56	64	30	22,140	397	18.1	30	97
8b	Sum(1+2+3+4 5b+6b+7b)	0.60	69	36	27,110	428	20.8	34	103
9	Gross concentration	0.66	67	35	28,560	381	18.2	32	94

*Average of two replicate analyses

Table 13

Trace Metal Partitioning among Geochemical Fractions

Element	Sta. #	Total trace metal (ppm) A	Non-residual fraction A	Non-residual fraction B	Biogenous fraction A	Biogenous fraction C	Nodular hydrogenous fraction A	Nodular hydrogenous fraction C	Non-nodular hydrogenous fraction A	Non-nodular hydrogenous fraction C	Residual (lithogenous) fraction A	Residual (lithogenous) fraction B
Cd	2	2.01	1.96	97.5	0.51	26.0	1.29	65.8	0.16	8.2	0.05	2.5
	6	1.98	1.72	85.9	0.74	43.5	0.89	52.4	0.07	4.1	0.28	14.1
	3	0.82	0.75	91.5	0.13	17.3	0.27	36.0	0.35	46.6	0.07	8.5
	4	0.60	0.57	95.0	0.07	12.0	0.15	27.6	0.35	60.3	0.03	5.0
Cr	2	175	68.1	38.9	5.0	7.3	51.7	75.9	11.4	16.8	107	61.1
	6	188	74.8	39.7	4.1	5.5	65.4	87.4	5.3	7.1	113	60.3
	3	97	30.8	32.1	3.0	9.7	23.8	77.3	4.0	12.9	66	67.9
	4	69	18.2	26.3	1.7	9.3	14.3	78.6	2.2	12.1	51	73.9
Cu	2	112	13.0	11.6	1.4	10.7	11.6	88.9	0.05	0.4	99	88.4
	6	880	11.4	1.4	4.0	35.0	7.4	64.6	0.04	0.40	869	98.6
	3	49	10.4	21.2	1.0	9.6	7.0	67.3	2.4	23.0	39	78.8
	4	36	11.6	32.1	1.0	8.6	5.6	48.2	5.0	43.1	24	67.9
Fe	2	42,610	9964	23.4	918	9.2	5088	51.1	3958	39.7	32,650	76.6
	6	40,550	10,320	25.4	720	7.0	4475	43.3	5126	49.7	30,220	74.5
	3	30,760	6113	19.9	659	10.8	3641	59.3	1833	29.9	24,630	80.1
	4	27,110	5008	18.5	567	11.3	3464	69.2	977	19.5	22,100	81.5

A = content, ppm

B = percent total trace metals

C = percent authigenic fraction

Station #2--sandy silt   #3--silty sand

#6--silty clay   #4--silty sand

Table 13, Concluded

Ele-ment	Sta. #	Total trace metal (ppm)	Non-residual fraction		Biogenic fraction		Nodular hydrogenous fraction		Non-nodular hydrogenous fraction		Residual (lithogenous) fraction	
			A	B	A	C	A	C	A	C	A	B
Mn	2	481	122	25.4	13.0	10.6	59	48.5	50	40.9	359	74.6
	6	455	104	23.0	11.0	10.5	54	52.0	39	37.5	350	77.0
	3	438	87	19.9	8.6	9.9	43	49.8	35	40.3	351	80.1
	4	428	72	17.0	7.4	10.2	40	54.6	25	35.2	356	83.0
Ni	2	42.7	15.7	36.8	3.7	23.6	9.3	59.2	2.7	17.2	27.0	63.2
	6	41.5	15.5	37.4	4.0	25.8	8.5	54.8	3.0	19.4	26.0	62.6
	3	23.7	8.2	34.7	1.7	20.7	5.0	60.8	1.5	18.5	15.5	65.3
	4	20.8	7.8	37.4	1.6	20.6	5.2	66.3	1.0	13.1	13.0	62.6
Pb	2	70	46	65.5	5.0	10.8	34	73.8	7.2	15.4	24	34.5
	6	342	177	51.8	42	23.7	134	75.7	1.0	0.6	165	48.2
	3	41	24.4	59.7	2.0	8.2	15	63.9	6.8	27.8	17	41.0
	4	34	20.2	59.0	1.8	8.9	13	64.3	5.4	26.8	14	41.0
Zn	2	227	143	63.0	34	24.1	65	45.5	44	30.7	84	37.0
	6	631	486	77.0	181	37.2	255	52.5	50	10.3	145	23.0
	3	125	72	57.7	12.0	16.6	30	41.6	30	41.8	53	42.3
	4	103	60	58.0	8.0	13.4	22	36.0	30	50.5	43	42.0

A = content, ppm
B = percent total trace metals
C = percent authigenic fraction

Station #2--sandy silt   #3--silty sand
#6--silty clay   #4--silty sand

Table 14

Column Test Series I: Water Quality of Soluble Phase in the Mixture of Seawater and Silty Clay Sediment (Sta. #6) under Quiescent Settling Conditions

Time Elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phos-phate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Sili-cate (mg/l)	Temp. °C
0	0.033	0.035	0.00	0.65	0.00	0.04	0.1	0.1	0.47	0.38	6.2	--	--	0.01	0.01	0.22	0.02	0.20	1.5	--
0.5	0.063	0.021	0.00	0.25	31.2	0.08	10.1	0.24	0.43	0.00	--	--	--	--	--	--	--	--	--	--
2	--	--	--	--	--	--	--	--	--	--	--	--	--	0.14	0.13	0.39	0.068	0.32	2.3	--
4	0.00	0.004	0.4	0.00	44.4	0.04	11.7	0.04	0.03	0.00	0.48	--	--	--	--	--	--	--	--	--
24	0.00	0.025	0.00	0.35	2.0	0.03	10.4	0.12	0.16	0.1	0.48	--	--	0.27	0.25	0.61	0.081	0.53	8.5	--
48	--	--	--	--	--	--	--	--	--	--	--	--	--	0.25	0.23	0.80	0.12	0.68	1.2	--
72	0.00	0.008	0.00	0.00	7.0	<0.02	10.8	0.09	4.0	0.00	0.21	--	--	--	--	--	--	--	--	--
Original sea-water	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

-- not determined

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Table 15

Column Test Series II: Water Quality of Soluble Phase in the Mixture of Seawater and Silty Sand Sediment (Sta. #3) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phosphate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Silicate (mg/l)	Temp °C
0	0.188	0.011	0.40	0.70	0.00	0.041	0.1	0.16	1.09	2.58	5.75	--	--	0.02	0.02	0.050	0.00	0.05	1.50	--
0.5	0.020	0.047	2.45	0.55	0.00	0.058	22.5	0.18	0.87	8.62	1.90	--	--	0.20	0.21	0.258	0.085	0.173	3.00	--
1	0.025	0.020	0.25	0.38	0.00	0.058	20.9	0.11	0.30	1.90	1.90	--	--	0.15	0.12	0.237	0.065	0.172	2.50	--
2	0.155	0.008	0.10	0.35	0.00	0.057	22.9	0.15	0.00	3.20	2.05	--	--	--	--	--	--	--	--	--
4	0.00	0.004	0.35	0.35	0.00	0.072	21.1	0.14	0.11	3.00	1.70	--	--	0.13	0.13	0.326	0.072	0.254	2.25	--
8	0.00	0.006	0.45	0.40	0.00	0.030	19.2	0.11	0.26	0.54	1.73	--	--	--	--	--	--	--	--	--
24	0.00	0.011	0.40	0.38	0.00	<0.02	18.8	0.15	0.38	6.69	1.58	7.53	--	0.12	0.12	0.349	0.061	0.288	9.50	--
48	0.020	0.012	0.00	1.00	0.00	--	--	0.10	0.53	0.12	0.94	7.65	--	0.17	0.16	0.386	0.062	0.324	9.60	--
96	--	--	--	--	--	--	--	--	--	--	--	--	--	0.11	0.10	0.430	0.064	0.366	10.1	--
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-8.0	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater 1:20 by volume

-- not determined

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Table 16

Column Test Series VIII: Water Quality of Soluble Phase in the Mixture of Seawater and Silty Clay Sediment (Sta. #6) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Phos-phate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Sili-cate (mg/1)	Temp °C
0	--	0.016	0.25	0.13	10	0.125	1.0	0.06	0.12	0.03	7.0	7.59	0.008	0.040	0.093	0.135	0.021	0.114	1.75	24.0
0.5	--	0.009	5.2	0.03	2000	0.026	19.3	0.13	0.052	0.51	0.0	8.15	2.76	1.050	0.890	0.643	0.182	0.461	10.65	23.5
1	--	0.05	0.8	0.08	480	0.051	5.5	0.065	0.051	0.84	0.0	8.17	0.108	0.455	0.430	0.421	0.097	0.324	12.20	24.0
2	--	0.04	0.6	0.07	118	<0.02	2.7	0.058	0.051	0.66	0.0	8.14	0.003	0.405	0.305	0.593	0.131	0.462	10.15	24.5
4	--	0.02	0.4	0.05	105	0.035	2.3	0.005	0.04	0.58	0.0	7.61	0.047	0.350	0.360	0.674	0.143	0.531	9.85	26.4
8	--	0.006	0.35	0.03	100	0.07	2.0	0.002	0.03	0.57	0.0	--	0.018	0.340	0.340	--	--	--	7.70	24.5
12	--	0.005	0.3	0.02	85	0.03	2.3	0.001	0.03	0.27	0.1	7.72	0.019	0.555	0.540	0.686	0.142	0.544	10.35	25.0
24	--	0.005	0.2	0.02	80	0.03	1.7	0.001	0.01	0.24	0.1	7.78	0.062	0.400	0.330	0.761	0.138	0.623	16.55	26.1
48	--	0.003	0.1	0.01	75	0.03	1.6	0.001	0.01	0.24	0.1	7.77	0.044	0.420	0.420	0.813	0.126	0.687	15.70	25.4
Original Seawater Background	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

-- not determined

135

Table 17

Column Test Series X: Water Quality of Soluble Phase in the Mixture of Seawater and Silty Sand Sediment (Sta. #3) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Phos- phate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Sili- cate (mg/1)	Temp °C
0	--	0.31	0.05	3.1	11.0	0.118	2.2	2.0	2.91	4.0	6.6	7.71	0.007	0.040	0.035	0.132	0.010	0.122	2.00	--
0.5	--	0.40	0.05	2.17	178	0.093	15.2	3.24	1.15	6.1	0.3	7.57	0.01	0.285	0.280	0.249	0.092	0.157	8.65	--
1	--	0.06	0.18	0.2	81.5	0.11	12.1	1.08	0.08	2.1	0.4	7.64	0.018	0.210	0.205	0.260	0.081	0.179	7.05	22.5
2	--	0.0	0.05	0.25	87.5	0.11	13.1	1.3	0.1	0.0	1.1	7.62	0.001	0.215	0.215	0.332	0.065	0.267	4.50	21.0
4	--	0.0	0.15	0.8	15.5	0.103	13.6	1.1	0.1	0.1	0.7	7.60	0.009	0.225	0.230	0.285	0.066	0.219	4.50	21.5
8	--	0.1	0.15	0.38	112	0.088	14.1	1.1	0.6	3.44	0.8	7.53	0.002	0.250	0.270	0.345	0.080	0.265	6.70	22.5
12	--	0.0	0.27	0.74	192	0.105	11.6	1.22	0.09	0.0	0.4	7.51	0.002	0.265	0.260	0.419	0.077	0.342	8.65	22.5
24	--	0.01	0.15	0.4	49.0	--	14.4	1.2	0.0	0.0	0.3	7.21	0.0	0.280	0.270	0.428	0.074	0.354	10.05	22.5
48	--	0.14	0.16	1.4	102	--	12.7	1.1	0.52	3.0	0.15	7.89	0.0	0.235	0.230	0.436	0.073	0.363	11.15	22.5
Original Seawater	<0.02	0.03- 0.24	0.05- 0.8	0.1- 0.8	0.4- 3.0	0.03- 0.15	0.4- 3.0	0.02- 0.75	0.03- 0.12	0.2- 0.5	6.8- 8.0	7.8- 8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 18

Column Test Series XII: Water Quality of Soluble Phase in the Mixture of Seawater and
Silty Sand Sediment (Sta. #1) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phosphate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Silicate (mg/1)	Temp °C
0	--	0.1	0.1	4.5	8.5	0.133	0.9	1.4	0.0	0.35	6.6	8.0	0.005	0.035	0.030	0.470	0.040	0.430	2.00	23.6
0.5	--	0.15	0.01	0.0	35.0	0.129	5.2	0.75	0.0	0.18	4.0	8.15	0.0	0.460	0.450	0.550	0.080	0.470	10.45	22.5
1	--	0.31	0.1	0.9	4.5	0.149	5.5	1.0	0.5	6.0	3.8	8.17	0.001	0.490	0.455	0.550	0.160	0.390	9.80	22.5
2	--	0.28	0.15	0.3	33.0	0.079	5.0	0.77	0.4	4.7	3.9	8.15	0.01	0.400	0.320	0.450	0.080	0.370	7.65	22.5
4	--	0.43	0.0	0.33	2.5	0.030	5.6	0.75	0.3	5.2	3.9	8.12	0.0	0.325	0.325	0.630	0.160	0.470	10.10	22.2
8	--	0.17	0.02	4.1	4.5	0.106	4.0	0.50	0.0	0.08	3.4	8.12	0.002	0.390	0.370	0.181	0.000	0.181	8.75	22.2
12	--	1.16	1.7	2.0	4.5	0.076	2.5	1.02	0.0	0.06	3.4	8.12	0.01	0.350	0.350	0.210	0.035	0.175	9.20	22.8
24	--	0.16	0.8	0.55	3.8	0.075	0.7	0.76	0.0	1.6	3.4	8.14	0.008	0.320	0.330	0.198	0.023	0.175	10.40	22.5
48	--	0.82	0.0	1.5	3.8	--	0.3	0.80	8.4	5.46	3.6	8.31	0.01	0.320	0.320	0.443	0.093	0.350	7.25	22.5
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

Table 19

Column Test Series XIV: Water Quality of Soluble Phase in the Mixture of Seawater and Sandy Silt Sediment (Sta. #2) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phosphate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Silicate (mg/l)	Temp °C
0	0.0	0.38	4.0	4.6	0.0	0.041	1.5	1.7	1.85	3.52	6.54	8.2	0.001	0.020	0.015	0.199	0.039	0.160	1.00	23.4
0.5	0.0	0.15	1.7	0.9	385	0.018	23.0	1.1	0.4	3.76	0.81	8.3	0.007	0.625	0.620	0.272	0.039	0.233	14.10	21.8
1	0.0	0.02	1.3	0.2	240	0.028	20.0	0.8	0.02	0.9	0.72	8.31	0.011	0.520	0.495	0.554	0.049	0.505	12.05	21.8
2	0.00	1.46	2.8	1.22	460	0.130	21.5	1.02	1.13	3.68	0.72	8.33	0.012	0.485	0.480	0.348	0.058	0.290	10.20	21.8
4	0.0	0.07	0.35	1.32	10	0.041	24.0	1.12	0.02	3.7	1.42	8.33	0.009	0.355	0.355	0.495	0.140	0.355	9.75	22.4
8	0.0	0.01	0.7	0.55	0.0	0.008	20.5	1.22	0.04	0.1	1.05	8.23	0.007	0.425	0.420	0.510	0.023	0.487	12.15	23.5
12	0.0	0.45	0.25	0.85	10	0.118	20.7	0.8	0.04	3.08	0.4	8.2	0.008	0.320	0.310	0.429	0.062	0.367	13.70	23.2
24	0.0	0.71	0.75	0.32	0.0	0.038	17.5	0.75	0.02	3.6	0.56	8.19	0.007	0.295	0.290	0.583	0.023	0.560	12.90	22.6
48	0.03	0.31	0.1	1.05	0.0	0.035	15.0	0.87	1.7	3.5	0.5	8.23	0.004	0.310	0.310	0.477	0.110	0.367	13.25	23.0
Original Seawater	< 0.02	0.03–0.24	0.05–0.8	0.1–0.8	0.4–3.0	0.03–0.15	0.4–3.0	0.02–0.75	0.03–0.12	0.2–0.5	6.8–8.0	7.8–8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 20

Column Test Series XVIII: Water Quality of Soluble Phase in the Mixture of
Seawater and Morris Dam Sediment under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phos-phate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Sili-cate (mg/l)	Temp °C
0	0.17	0.21	2.2	4.9	0.0	0.061	30.0	6.5	1.9	4.3	6.60	8.32	0.005	0.040	0.036	0.443	0.132	0.311	1.50	23.6
0.5	0.24	0.90	11.38	2.1	130	0.021	95.0	2.1	5.2	3.9	1.0	8.18	0.006	0.025	0.023	0.754	0.054	0.700	10.30	22.7
1	0.19	0.17	1.0	2.4	120	0.976	95.0	2.7	1.7	0.5	0.80	8.18	0.002	0.015	0.013	0.483	0.093	0.390	8.40	22.7
2	0.14	0.82	1.0	1.7	45.0	0.194	95.0	2.2	2.0	4.4	1.0	8.18	0.008	--	--	0.396	0.086	0.310	8.00	23.8
4	0.07	0.17	1.0	0.9	0.0	0.051	95.0	1.0	1.5	4.3	0.90	8.19	0.01	0.065	0.063	0.308	0.078	0.230	7.6	24.0
8	0.09	0.2	2.1	1.2	0.0	0.103	98.0	1.3	1.4	4.1	0.90	8.40	0.002	0.062	0.060	0.440	0.070	0.370	5.80	24.2
12	0.25	0.54	1.3	6.4	0.0	0.288	95.0	1.7	1.05	4.45	0.95	7.83	0.001	0.055	0.055	0.447	0.117	0.33	5.90	23.4
24	0.11	0.29	0.5	0.9	0.0	0.056	95.0	1.4	1.0	3.15	0.85	7.82	0.001	0.068	0.060	0.612	0.132	0.480	4.80	23.9
48	0.26	0.02	1.0	1.4	0.0	0.075	96.0	1.45	0.2	1.7	0.80	7.88	0.015	0.015	0.010	0.509	0.109	0.400	4.80	23.5
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 21

Column Test Series XX: Water Quality of Soluble Phase in the Mixture of Freshwater and Morris Dam Sediment under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total Sulfide (mg/1)	Total phosphorus (mg/1)	Phosphate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Silicate (mg/1)	Temp °C
0	0.0	0.35	5.8	2.6	0.0	0.066	5.0	2.2	0.5	4.0	2.3	7.57	0.005	0.055	0.055	0.292	0.062	0.23	21.00	22.4
0.5	0.0	1.45	2.5	4.0	5.0	0.065	189	3.8	2.7	3.1	2.0	7.38	0.008	0.095	0.080	0.643	0.023	0.62	22.72	21.7
1	0.12	0.45	1.6	2.0	0.0	0.073	188	1.3	1.6	3.11	1.4	7.36	0.002	0.220	0.173	0.451	0.031	0.42	7.84	22.5
2	0.0	0.4	1.0	1.8	0.0	0.045	181	1.4	0.52	2.45	1.3	7.37	0.009	0.175	0.161	0.393	0.023	0.37	8.08	22.0
4	0.0	0.4	1.0	1.8	0.0	0.022	192	1.55	0.22	3.15	1.3	7.41	0.009	0.225	0.202	0.322	0.042	0.28	6.66	22.1
8	0.09	0.5	0.8	1.7	15.0	0.04	175	1.37	0.9	4.1	1.7	7.36	0.01	0.130	0.117	0.150	--	0.15	11.68	22.4
12	0.0	0.63	1.0	2.35	0.0	0.058	164	2.0	4.95	4.1	2.3	7.37	0.004	0.110	0.100	0.258	0.028	0.23	11.84	22.0
24	0.0	0.52	0.7	2.45	20.0	--	127	1.7	0.2	4.3	2.2	7.37	0.008	0.140	0.138	0.427	0.037	0.39	5.8	21.8
48	0.00	0.3	0.4	2.4	0.0	0.006	64.0	2.3	0.7	4.2	2.2	7.73	0.008	0.110	0.107	0.325	0.015	0.31	4.4	21.3
Original Seawater	< 0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

Table 22

Column Test Series III: Water Quality of Soluble Phase in the Mixture of Deaerated Seawater and Silty Clay Sediment (Sta.#6) with N_2 Bubbling under Quiescent Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Phosphate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Silicate (mg/1)	Temp °C
0	--	0.00	0.28	1.05	0.00	--	--	0.21	0.00	1.67	2.75	7.66	--	0.02	0.02	0.120	0.020	0.100	1.05	--
0.5	--	--	--	--	--	--	--	--	--	--	0.00	7.76	--	0.37	0.36	0.547	0.124	0.423	7.75	--
24	0.00	0.00	0.28	0.35	30.0	--	--	0.05	0.00	19.8	0.00	8.35	--	--	--	--	--	--	--	--
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00							

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 23

Column Test Series IV: Water Quality of Soluble Phase in the Mixture of Deaerated
Seawater and Silty Sand Sediment (Sta. #3) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phos-phate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Sili-cate (mg/l)	Temp °C
0	0.01	0.213	0.15	1.03	0.0	--	1.6	0.08	0.44	2.0	0.4	8.61	0.0	0.020	0.015	0.120	0.020	0.100	1.00	--
0.5	0.03	0.002	0.0	0.65	1070	<0.02	11.2	0.07	0.32	0.5	0.5	7.94	0.003	0.440	0.430	0.498	0.132	0.366	10.50	--
1	0.0	0.0	0.30	2.48	1050	--	23.2	0.24	0.0	0.5	0.2	7.56	0.004	0.430	0.415	0.343	0.129	0.214	2.65	--
2	--	0.006	0.0	1.18	1045	0.035	26.4	0.03	0.10	1.6	0.9	8.39	0.006	0.430	0.430	0.379	0.091	0.288	2.60	--
4	--	0.008	0.0	1.23	1075	0.041	22.8	0.22	0.0	1.4	0.3	8.45	0.008	0.460	0.455	0.320	0.088	0.232	2.90	--
8	0.01	0.010	0.0	0.90	1050	0.050	14.8	0.04	0.0	1.0	0.6	8.35	0.0	0.490	0.470	0.482	0.066	0.416	5.35	--
12	--	0.0	0.31	1.02	1070	0.065	14.0	0.05	0.0	0.4	0.1	8.36	0.017	0.490	0.470	0.497	0.073	0.424	8.20	--
24	0.0	0.0	0.0	0.43	970	0.165	18.4	0.04	0.0	0.2	0.0	8.27	0.062	0.470	0.470	0.484	0.074	0.410	13.20	--
48	0.0	0.007	0.0	0.13	908	0.190	20.4	0.03	0.0	0.3	0.1	7.38	0.0	0.440	0.430	0.503	0.079	0.424	15.15	--
Original Sea-water	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

-- not determined

Table 24

Column Test Series VII: Water Quality of Soluble Phase in the Mixture of Deaerated Seawater and Silty Clay Sediment (Sta. #6) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phos-phate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Sili-cate (mg/l)	Temp °C
0	0.02	0.315	0.35	3.65	5.1	0.064	0.08	5.38	2.04	5.45	0.40	7.78	0.05	0.01	0.013	0.120	0.015	0.105	1.05	--
0.5	0.018	0.137	0.95	2.0	9.5	<0.02	0.35	4.78	1.13	6.6	0.0	8.01	4.02	0.65	0.555	0.864	0.365	0.499	15.3	--
1	0.018	0.095	0.95	0.25	43.0	0.008	0.83	4.38	0.78	5.6	0.0	7.34	4.72	0.605	0.535	0.674	0.253	0.421	14.1	--
2	0.018	0.075	1.0	0.02	8.0	0.040	0.60	4.9	0.45	5.3	0.0	7.32	2.76	0.61	0.613	0.779	0.288	0.491	13.0	--
4	0.017	0.020	0.95	0.02	10.0	0.028	0.52	4.9	0.45	3.5	0.0	7.18	4.34	0.61	0.540	0.846	0.223	0.623	13.6	--
8	0.018	0.001	0.65	0.0	27.0	0.031	3.25	4.9	0.45	2.8	0.0	7.41	5.50	0.60	0.540	0.835	0.213	0.622	13.3	--
12	0.018	0.001	0.35	0.0	8.0	0.030	0.32	2.98	0.44	2.2	0.0	--	--	0.60	0.580	0.896	0.275	0.621	10.1	--
24	0.018	0.001	0.35	0.25	10.0	0.029	0.70	2.72	0.44	0.3	0.0	7.73	4.76	0.57	0.550	0.882	0.239	0.643	12.2	--
48	0.017	0.001	0.35	1.77	7.5	0.029	0.65	4.8	0.43	0.3	0.0	7.56	4.28	0.58	0.550	0.926	0.216	0.710	13.1	--
Original Sea-water	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.0	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 25

Column Test Series XVI: Water Quality of Soluble Phase in the Mixture of Deaerated
Seawater and Sandy Silt Sediment (Sta. #2) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Phosphate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Silicate (mg/1)	Temp °C
0	0.007	0.47	0.3	6.6	0.0	0.148	1.5	9.0	5.6	5.9	0.35	8.33	0.011	0.020	0.015	0.520	0.108	0.412	1.50	23.8
0.25	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.395	--	--	--	--	--
0.5	0.007	0.69	0.8	1.75	495	0.049	16.5	0.0	0.35	5.0	0.0	8.14	0.025	0.455	0.450	0.401	0.070	0.133	17.15	23.2
1	0.008	0.79	0.5	0.6	470	0.051	16.6	0.9	1.7	4.6	0.05	8.14	0.021	0.405	0.395	0.438	0.147	0.291	16.45	23.8
2	0.012	0.54	0.9	0.57	485	0.094	16.6	0.35	1.2	3.95	0.1	8.14	0.025	0.290	0.280	0.438	0.147	0.291	14.15	24.0
4	0.015	0.51	1.15	0.63	480	0.121	19.7	0.15	0.4	1.87	0.15	8.13	0.025	0.285	0.290	0.353	0.155	0.198	17.25	24.5
8	0.015	0.65	0.25	0.15	470	0.054	12.0	0.50	0.6	5.7	0.35	8.14	0.021	0.325	0.320	0.478	0.090	0.388	14.35	25.7
12	0.015	0.52	1.2	0.4	495	0.085	15.5	0.25	1.1	5.2	0.45	8.14	0.02	0.355	0.350	0.820	0.031	0.789	18.75	25.7
24	0.015	0.01	0.75	0.7	320	0.035	15.2	0.15	0.0	0.2	0.30	8.09	0.02	0.380	0.375	0.720	0.171	0.549	19.45	25.2
48	0.017	0.3	0.7	0.1	20	0.056	15.0	0.35	0.7	3.6	0.55	8.00	0.0	0.390	0.425	0.204	0.204	--	20.10	24.3
Original Seawater	< 0.02	0.03- 0.24	0.05- 0.8	0.1- 0.8	0.4- 3.0	0.03- 0.15	0.4- 3.0	0.02- 0.75	0.03- 0.12	0.2- 0.5	6.8- 8.0	7.8- 8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 26

Column Test Series XIX: Water Quality of Soluble Phase in the Mixture of Deaerated
Seawater and Morris Dam Sediment under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total Sulfide (mg/l)	Total Phosphorus (mg/l)	Phos-phate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Sili-cate (mg/l)	Temp °C
0	0.3	0.34	1.0	9.0	0.0	0.13	11.0	3.0	0.6	4.4	0.2	8.43	0.011	0.068	0.065	1.250	0.390	0.86	1.6	22.9
0.5	0.3	0.22	0.5	1.1	260	0.04	95.6	0.5	0.65	4.3	0.10	8.35	0.009	0.025	0.015	1.55	0.62	0.93	15.30	23.2
1	0.0	0.35	0.5	1.0	260	0.014	95.4	1.9	0.9	4.42	0.10	8.55	0.0	--	--	1.38	0.46	0.92	16.0	23.5
2	0.5	0.07	0.75	1.05	230	0.029	95.3	2.0	0.5	4.35	0.10	7.87	0.005	0.035	0.032	1.37	0.38	0.93	16.4	24.0
4	0.8	0.22	0.5	1.1	240	0.037	95.2	1.7	0.8	4.45	0.10	7.79	0.015	0.015	0.013	1.32	0.31	1.01	16.6	24.4
8	0.2	0.31	0.5	0.93	225	0.041	96.5	1.75	0.6	4.44	0.10	8.08	0.009	0.080	0.070	1.04	0.27	0.77	8.8	24.0
12	0.0	0.1	1.0	0.75	227	0.207	95.0	0.7	0.5	4.0	0.10	8.01	0.025	0.040	0.035	0.97	0.27	0.70	7.4	23.9
24	0.25	0.34	0.5	5.55	175	0.078	96.5	2.0	1.1	3.65	0.10	8.3	0.008	0.047	0.045	0.94	0.27	0.67	7.0	23.5
48	0.02	0.17	0.5	1.2	75.0	0.155	96.5	2.4	2.87	4.3	0.15	8.40	0.015	0.085	0.080	1.23	0.38	0.85	12.4	23.5
Original Seawater	< 0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

-- not determined

145

Table 27

Column Test Series XXI: Water Quality of Soluble Phase in the Mixture of Deaerated Freshwater and Norris Dam Sediment under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phosphate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Silicate (mg/l)	Temp °C
0	0.1	0.52	0.4	1.1	0.0	0.038	0.0	1.9	1.0	3.35	0.20	7.58	0.015	0.065	0.060	0.510	0.110	0.400	15.00	22.0
0.5	0.1	0.46	0.4	0.9	10.0	0.051	165	1.75	0.5	2.7	0.10	7.55	0.012	0.130	0.110	0.419	0.080	0.339	11.83	22.0
1	0.0	1.05	0.4	1.3	19.0	0.046	170	1.05	1.7	4.1	0.10	7.61	0.01	0.095	0.087	0.443	0.133	0.310	9.73	22.0
2	0.1	0.15	0.4	0.7	3.0	0.024	188	0.55	1.0	4.2	0.10	7.61	0.01	0.085	0.081	0.438	0.140	0.298	7.90	22.0
4	0.0	0.22	3.4	0.1	23.0	0.056	195	0.45	1.15	3.05	0.10	7.50	0.015	0.078	0.077	0.380	0.105	0.275	6.94	22.0
8	0.01	0.2	0.6	0.4	11.0	0.052	181	0.4	0.6	4.1	0.15	7.54	0.011	0.130	0.103	0.485	0.097	0.388	5.83	21.9
12	0.1	0.58	0.4	0.4	28.0	0.045	200	1.2	0.5	3.0	0.10	7.44	0.012	0.110	0.098	0.279	0.081	0.198	4.74	23.2
24	0.1	0.2	0.4	0.4	0.0	0.002	193	0.8	0.2	3.7	0.20	7.58	0.01	0.110	0.103	0.415	0.180	0.235	4.98	21.8
48	0.1	0.58	0.4	0.3	7.0	0.033	193	0.85	0.55	3.75	0.20	7.90	0.01	0.08	0.064	0.729	0.191	0.538	5.02	23.0
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

146

Table 28

Column Test Series VI: Water Quality of Soluble Phase in the Mixture of Oxygen Aerated Seawater and Silty Clay Sediment (Sta. #6) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phosphate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Silicate (mg/l)	Temp °C
0	0.01	0.62	0.35	3.6	5.0	0.157	0.12	2.9	4.0	9.5	7.1	8.02	0.09	0.02	0.013	0.231	0.021	0.210	1.80	--
0.5	0.0	0.55	0.35	1.25	25	<0.02	2.40	3.6	1.25	8.4	0.0	7.93	0.112	0.47	0.455	0.652	0.200	0.452	12.2	--
1	0.0	0.14	0.22	1.0	132	0.145	1.77	0.6	0.2	10.1	0.0	7.94	0.073	0.41	0.380	0.496	0.154	0.342	13.45	--
2	0.0	0.35	0.18	1.45	128	<0.02	0.85	1.0	3.1	5.72	0.1	7.82	0.082	0.45	0.463	--	--	--	10.8	--
4	0.0	0.15	0.0	0.97	87	0.126	0.80	0.8	0.4	10.1	0.0	7.92	0.06	0.435	0.430	0.776	0.156	0.620	10.2	--
8	0.0	0.12	0.78	1.75	102	0.126	0.85	0.4	0.95	2.9	0.0	7.52	0.061	0.48	0.480	0.685	0.142	0.543	8.10	--
12	0.0	0.02	0.35	0.38	107	0.110	1.00	0.5	1.82	0.9	0.0	7.71	0.062	0.48	0.470	--	0.123	--	7.65	--
24	0.0	0.06	0.55	0.42	80	0.020	1.67	0.4	0.87	5.3	0.0	7.90	0.105	0.46	0.450	0.754	0.133	0.621	12.4	--
48	0.0	0.09	0.35	0.51	128	--	0.42	0.3	0.3	1.35	0.0	7.56	0.106	0.47	0.450	0.695	0.135	0.560	14.2	--
Original seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment: seawater ~ 1:20 by volume

--not determined

147

Table 29

Column Test Series XXIII: Water Quality of Soluble Phase in the Mixture of Compressed
Air Aerated Seawater and Silty Sand Sediment (Sta. #3) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phos- phate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Sili- cate (mg/l)	Temp °C
0	--	0.5	0.47	3.75	0.0	0.39	1.1	1.4	1.3	5.6	7.8	8.66	0.001	0.105	0.092	0.28	0.041	0.239	1.70	19.8
0.5	--	0.0	0.4	1.2	75.0	1.33	2.4	0.9	0.4	4.5	1.84	8.77	0.015	0.110	0.087	0.584	0.197	0.387	10.50	20.3
1	--	0.0	0.4	0.5	75.0	0.5	7.7	0.6	0.5	6.4	1.90	8.81	0.01	0.065	0.055	0.513	0.163	0.350	12.60	20.0
2	--	0.1	0.45	0.6	35.0	2.18	2.55	0.9	0.7	4.8	1.1	8.80	0.012	0.040	0.030	0.535	0.155	0.38	10.80	20.0
4	--	0.12	0.37	0.8	40.0	1.33	2.7	0.9	0.4	5.5	1.9	8.50	0.012	0.045	0.033	0.695	0.160	0.535	10.20	20.1
8	--	0.1	0.43	0.9	0.0	0.02	2.3	0.8	1.0	4.6	1.6	8.56	0.009	0.042	0.032	0.697	0.143	0.554	8.6	21.0
12	--	0.13	0.37	0.65	0.0	0.209	2.35	0.65	0.6	6.8	1.5	8.70	0.00	0.08	0.066	0.866	0.135	0.731	7.8	20.0
24	--	0.1	0.5	1.25	0.0	0.033	3.1	1.1	0.6	5.5	1.5	8.69	0.016	0.065	0.042	0.820	0.130	0.690	12.90	20.8
48	--	0.08	0.45	0.9	0.0	--	2.4	1.1	0.4	5.7	1.5	8.62	0.015	0.055	0.029	0.650	0.129	0.521	13.9	21.0
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

148

Table 30

Column Test Series XIV: Water Quality of Soluble Phase in the Mixture of Aerated Seawater and Sandy Silt Sediment (Sta. #6) under Quiescent Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phosphate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Silicate (mg/l)	Temp °C
0	--	0.3	1.9	1.8	0.0	1.022	2.4	2.0	2.5	5.8	7.2	8.6	0.001	0.035	0.041	0.316	0.050	0.266	1.60	20.3
0.5	--	0.01	1.5	1.0	17.0	0.182	3.0	3.1	2.1	5.5	2.7	8.48	0.002	0.110	0.083	0.600	0.210	0.390	12.20	19.7
1	--	0.08	0.82	0.7	8.0	0.162	2.8	2.6	0.6	5.3	2.2	8.48	0.005	0.055	0.041	0.561	0.174	0.387	14.10	20.2
2	--	0.0	0.8	0.4	0.0	0.026	2.2	0.4	3.4	5.0	2.1	8.48	0.005	0.070	0.059	0.572	0.16	0.412	10.8	20.0
4	--	0.0	0.7	3.4	0.0	0.164	2.1	2.6	3.1	5.2	2.1	8.68	0.008	0.070	0.059	0.690	0.177	0.513	9.9	20.4
8	--	0.87	0.9	2.2	0.0	1.78	1.9	3.5	2.5	4.8	2.1	8.41	0.011	0.065	0.040	0.718	0.159	0.559	9.10	20.2
12	--	0.0	1.0	0.5	4.0	0.156	1.7	1.8	2.8	5.9	1.9	8.48	0.01	0.055	0.032	0.776	0.143	0.633	8.60	20.4
24	--	0.0	1.05	0.9	10.0	0.3	1.6	1.5	1.2	6.7	2.0	8.57	0.01	0.080	0.059	0.720	0.130	0.590	11.90	20.2
48	--	1.2	0.7	0.36	9.0	0.3	1.45	0.5	1.4	5.05	2.0	8.53	0.01	0.055	--	0.673	0.110	0.563	13.20	20.0
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

149

Table 31

Column Test Series V: Water Quality of Soluble Phase in the Mixture of Deaerated
Seawater and Silty Sand Sediment (Sta. #3) under Agitated Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phosphate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Silicate (mg/l)	Temp °C
0	0.01	0.213	0.15	1.03	0.0	--	1.6	0.08	0.44	2.0	0.6	8.82	0.0	0.02	0.015	0.120	0.020	0.100	1.00	--
0.5	0.02	0.086	0.45	0.90	790	0.062	26.6	0.16	0.08	3.1	0.0	8.56	0.002	0.41	0.405	0.522	0.120	0.402	10.3	--
1	0.0	0.0	0.26	0.89	822	<0.02	25.6	0.20	0.30	0.4	0.0	8.57	0.022	0.34	0.330	0.372	0.122	0.250	2.70	--
2	0.0	0.005	0.15	0.60	550	0.032	22.6	0.01	0.0	0.4	0.0	8.54	0.0	0.38	0.380	0.405	0.081	0.324	2.70	--
4	0.05	0.032	2.80	1.48	980	0.023	31.6	0.14	1.32	1.6	0.0	8.62	0.050	0.37	0.373	0.464	0.064	0.400	2.70	--
8	0.03	0.053	1.30	1.48	515	0.041	28.0	0.13	1.26	3.8	0.0	8.73	0.037	0.38	0.373	0.482	0.079	0.403	5.10	--
12	--	0.0	0.15	0.95	72	0.061	23.1	0.06	0.0	0.2	0.0	8.10	--	0.42	0.415	0.482	0.080	0.402	7.40	--
24	0.01	0.075	0.32	1.04	190	0.019	20.4	0.22	0.0	0.8	0.0	8.08	0.022	0.43	0.410	0.511	0.079	0.432	12.30	--
48	--	0.007	0.0	0.65	62	0.020	20.5	0.04	0.15	0.3	0.0	8.10	0.001	0.43	0.415	0.538	0.076	0.462	14.10	--
Original seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.12	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment ~ seawater: 1:20 by volume

--not determined

150

Table 32

Column Test Series XIII: Water Quality of Soluble Phase in the Mixture of Deaerated Seawater and Silty Sand Sediment (Sta. #1) under Agitated Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Phos-phate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Silicate (mg/1)	Temp °C
0	--	0.41	0.0	4.7	4.5	0.531	0.0	0.85	0.52	3.2	0.5	8.35	0.009	0.025	0.020	0.140	0.035	0.105	2.10	21.6
0.5	--	0.15	0.03	0.8	58.5	0.087	5.0	0.69	0.5	4.1	0.0	8.16	0.002	0.570	0.560	0.315	0.140	0.175	10.35	22.5
1	--	0.62	0.02	2.35	87.5	0.336	6.2	1.07	0.7	4.4	0.0	8.28	0.035	0.525	0.505	0.362	0.012	0.350	14.20	22.5
2	--	0.64	0.0	0.71	59.0	0.159	6.4	0.7	0.48	3.9	0.0	8.29	0.001	0.490	0.470	0.408	0.000	0.408	9.75	22.5
4	--	--	--	--	--	--	--	--	--	--	--	--	--	0.450	0.505	0.327	0.016	0.311	11.45	22.2
8	--	0.21	0.17	2.15	85.5	0.240	6.3	3.3	0.86	4.0	0.0	8.39	0.003	--	--	--	--	--	--	--
12	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
24	--	0.13	0.2	1.0	11.5	0.005	5.8	1.2	0.4	4.6	0.0	8.50	0.0	0.450	0.450	0.377	0.000	0.377	12.90	22.2
48	--	1.08	0.0	1.2	4.5	0.029	3.8	1.1	0.6	5.2	0.0	8.89	0.0	0.440	0.430	--	--	--	16.40	22.6
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

151

Table 33

Column Test Series XV: Water Quality of Soluble Phase in the Mixture of Deaerated
Seawater and Sandy Silt Sediment (Sta. #2) under Agitated Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Total Phos-phate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Sili-cate (mg/1)	Temp °C
0	0.0	0.12	1.35	11.4	405	0.381	26.0	1.8	1.0	4.8	0.56	8.34	0.005	0.020	0.015	0.583	0.140	0.443	1.50	23.5
0.25	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.480	--	--	--	--	--
0.5	0.0	0.28	1.2	2.5	430	0.065	21.0	1.1	1.1	4.6	0.0	8.28	0.012	0.455	0.440	0.121	0.020	0.101	15.20	22.4
1	0.0	0.0	0.25	3.1	220	0.041	20.5	0.7	0.0	0.2	0.0	8.31	0.05	0.370	0.370	0.443	0.040	0.443	17.10	22.4
2	0.015	0.05	0.8	2.2	230	0.106	19.5	0.55	0.0	0.3	0.0	8.31	0.009	0.370	0.355	0.070	0.070	--	14.35	22.4
4	0.0	0.1	1.0	1.9	195	0.184	19.0	1.25	0.6	4.0	0.0	8.37	0.045	0.345	0.325	0.272	--	0.272	16.45	23.1
8	0.0	0.02	0.8	1.0	105	0.059	18.0	1.0	0.0	0.6	0.0	8.45	0.01	0.330	0.320	0.193	0.078	0.115	15.15	23.0
12	0.0	0.13	0.0	1.6	23	0.066	15.5	2.1	0.45	4.5	0.0	8.51	0.028	0.375	0.370	0.295	0.078	0.217	16.20	21.8
24	0.0	0.06	0.0	1.75	60	--	16.2	1.1	0.93	0.55	0.0	8.58	0.011	0.375	0.360	0.503	0.272	0.231	16.95	22.0
48	0.015	0.32	0.17	2.24	21	--	22.5	1.1	0.1	0.25	0.0	8.6	0.011	0.380	0.375	0.330	0.117	0.213	17.45	23.0
Original Seawater	< 0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

-- not determined

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Table 34

Column Test Series XXII: Water Quality of Soluble Phase in the Mixture of Deaerated Seawater and Silty Clay Sediment (Sta. #6) under Agitated Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Total phosphate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Sili-cate (mg/1)	Temp °C
0	--	0.09	0.47	5.45	10.0	0.224	0.47	2.6	2.8	6.0	0.2	8.52	0.05	0.125	0.093	0.172	0.012	0.160	1.90	18.0
0.5	--	0.05	0.47	1.10	1950	0.033	1.2	3.3	2.75	5.8	0.1	8.50	0.06	0.224	0.188	0.242	0.012	0.230	20.05	18.0
1	--	0.07	0.42	0.70	190	0.023	1.4	1.2	3.6	6.0	0.1	8.60	0.055	0.319	0.294	0.162	0.012	0.150	17.50	17.5
2	--	0.1	0.47	1.50	155	0.209	0.9	1.35	3.3	5.9	0.1	8.64	0.07	0.350	0.332	0.262	0.012	0.250	15.40	18.1
4	--	0.02	0.47	1.30	170	0.12	1.6	0.7	4.2	5.8	0.1	8.70	0.074	0.239	0.199	0.552	0.012	0.540	16.30	17.9
8	--	0.15	0.5	1.20	30.0	0.038	1.0	0.67	1.5	6.2	0.15	8.81	0.088	0.335	0.301	0.643	0.023	0.620	13.30	17.5
12	--	0.10	0.48	1.52	20.0	0.07	1.1	1.15	1.43	6.2	0.1	8.87	0.05	0.314	0.312	0.828	0.058	0.770	16.40	17.0
24	--	0.10	0.47	1.61	17.0	0.064	1.05	0.5	1.8	6.2	0.2	8.98	0.048	0.343	0.324	0.755	0.035	0.720	16.80	17.6
48	--	0.09	0.47	1.10	40.0	--	1.4	1.7	1.7	6.2	0.2	8.99	0.054	0.302	0.290	0.730	0.070	0.660	17.70	17.5
Original Seawater	< 0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 35

Column Test Series IX: Water Quality of Soluble Phase in the Mixture of Compressed
Air Aerated Seawater and Silty Clay Sediment (Sta.#6) under Agitated Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/l)	pH	Total sulfide (mg/l)	Total phosphorus (mg/l)	Phos-phate (mg/l)	Kjeldahl nitrogen (mg/l)	Ammonia nitrogen (mg/l)	Organic nitrogen (mg/l)	Sili-cate (mg/l)	Temp °C
0	--	0.011	0.55	0.15	10.0	0.048	0.4	0.002	0.33	0.3	6.7	7.78	0.029	0.035	0.030	0.116	0.015	0.101	2.05	25.0
0.5	--	0.002	1.3	0.07	10.0	0.079	1.5	0.07	0.0	2.13	0.0	7.86	0.0	0.290	0.285	0.548	0.95	0.453	8.75	25.0
1	--	0.006	0.25	0.0	88.0	0.088	9.0	0.09	0.03	1.99	0.4	7.84	0.004	0.140	0.135	--	--	--	9.20	25.5
2	--	0.008	0.25	0.05	11.0	0.056	6.15	0.03	0.05	1.81	3.45	7.80	0.006	0.045	0.045	0.379	0.091	0.288	10.40	25.2
4	--	0.013	0.27	0.0	11.0	0.053	5.16	0.035	0.10	1.73	5.10	7.86	0.0	0.035	0.030	0.482	0.090	0.392	8.25	25.0
8	--	0.014	0.26	0.2	10.0	0.055	4.15	0.04	0.13	1.83	6.28	7.92	0.002	0.030	0.020	--	0.085	--	7.65	25.0
12	--	0.016	0.25	0.33	10.0	0.02	3.40	0.08	0.23	2.0	6.4	8.22	0.01	0.030	0.020	0.547	0.063	0.484	9.75	2.55
24	--	0.018	0.23	0.48	10.0	0.023	2.68	0.12	0.23	2.06	6.6	8.31	0.006	0.050	0.045	0.655	0.074	0.581	11.10	24.5
48	--	0.08	0.2	0.41	10.0	0.041	2.55	0.12	0.38	2.56	6.7	8.13	0.015	0.040	0.035	0.715	0.061	0.654	12.20	25.0
Original Seawater Background	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.4-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

-- not determined

Table 36

Column Test Series XI: Water Quality of Soluble Phase in the Mixture of Compressed
Air Aerated Seawater and Silty Sand Sediment (Sta. #3) under Agitated Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphorus (mg/1)	Phos-phate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Sili-cate (mg/1)	Temp °C
0	--	0.03	0.3	3.85	5.05	0.513	0.9	1.25	1.05	2.5	7.3	7.88	0.004	0.035	0.030	0.135	0.010	0.125	2.10	23.0
0.5	--	0.1	0.7	1.3	12.5	--	14.5	1.7	0.6	2.9	0.05	7.73	0.002	0.170	0.170	0.249	0.044	0.205	10.20	21.8
1	--	0.14	0.15	0.9	2.95	--	9.5	1.1	0.5	2.35	3.4	7.64	0.018	0.080	0.073	0.238	0.033	0.205	8.75	21.5
2	--	0.19	0.1	0.8	9.5	0.055	9.1	0.52	0.28	1.8	5.2	7.62	0.075	0.115	0.110	--	0.036	--	6.20	21.4
4	--	0.05	0.27	0.7	35.5	0.130	11.1	0.31	0.35	1.5	6.7	7.88	0.002	0.055	0.065	0.240	0.035	0.205	7.65	22.2
8	--	0.07	0.08	0.5	1.5	--	2.1	0.48	0.2	2.52	6.8	7.81	0.007	0.100	0.085	0.246	0.037	0.209	11.45	22.5
12	--	0.27	0.1	4.8	5.05	0.048	2.3	1.7	0.3	2.2	6.8	7.96	0.016	0.070	0.065	--	0.039	--	10.20	22.2
24	--	0.2	0.2	2.15	4.5	0.083	0.4	0.48	0.25	1.1	6.4	8.01	0.01	0.050	0.053	0.336	0.042	0.294	8.90	22.4
48	--	0.055	0.05	3.0	17.5	0.030	0.1	0.5	0.31	2.7	7.3	8.60	0.01	0.043	0.040	0.367	0.047	0.320	9.75	22.5
Original Seawater	<0.02	0.03-0.24	0.05-0.8	0.1-0.8	0.4-3.0	0.03-0.15	0.1-3.0	0.02-0.75	0.03-0.12	0.2-0.5	6.8-8.0	7.8-8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 37

Column Test Series XVII: Water Quality of Soluble Phase in the Mixture of Aerated
Seawater and Sandy Silt Sediment (Sta. #2) under Agitated Settling Conditions

Time elapsed (hrs)	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Dissolved oxygen (mg/1)	pH	Total sulfide (mg/1)	Total phosphor-us (mg/1)	Phos-phate (mg/1)	Kjeldahl nitrogen (mg/1)	Ammonia nitrogen (mg/1)	Organic nitrogen (mg/1)	Sili-cate (mg/1)	Temp °C
0	0.0	2.52	1.4	8.5	0.0	0.075	0.1	7.1	3.9	1.5	6.8	8.25	0.0	0.020	0.013	0.128	0.013	0.115	1.50	24.0
0.25	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.175	--	--	--	--	--
0.5	0.0	0.14	1.4	1.05	24.0	0.105	14.5	2.0	1.8	10.1	0.0	8.38	0.012	0.210	0.205	0.290	0.070	0.220	9.75	24.0
1	0.0	0.16	0.8	1.05	55.0	0.115	13.0	1.6	1.05	11.0	2.5	8.41	0.015	0.190	0.170	0.285	0.065	0.220	8.15	24.1
2	0.0	0.0	0.25	0.87	0.0	0.036	12.5	1.53	0.15	3.3	5.0	8.41	0.002	0.030	0.075	0.346	0.068	0.278	9.20	24.3
4	0.0	0.03	0.1	0.62	0.0	0.044	12.6	1.6	1.0	12.4	5.8	8.43	0.022	0.045	0.040	0.283	0.073	0.210	9.95	24.8
8	0.0	0.0	1.4	2.3	245	0.163	56.0	1.6	0.3	1.3	6.0	8.45	0.008	0.015	0.015	0.278	0.069	0.209	12.20	25.0
12	0.0	0.25	0.3	1.8	0.0	0.133	9.0	1.8	0.7	11.7	6.7	8.44	0.032	0.005	0.005	0.460	0.074	0.386	9.75	24.5
24	0.0	0.18	0.1	1.9	0.0	0.083	2.7	3.6	1.5	12.7	6.6	8.58	0.021	0.065	0.060	0.411	0.080	0.331	10.15	24.5
48	0.0	0.68	0.23	8.5	0.0	0.100	4.0	3.3	1.8	13.0	6.8	8.8	0.012	0.055	0.050	0.358	0.067	0.291	10.15	24.5
Original Seawater	<0.02	0.03–0.24	0.05–0.8	0.1–0.8	0.4–3.0	0.03–0.15	0.4–3.0	0.02–0.75	0.03–0.12	0.2–0.5	6.8–8.0	7.8–8.0	0.00	--	--	--	--	--	--	--

Trace metals in ppb

Sediment/seawater ~ 1:20 by volume

--not determined

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Table 38

Dissolved Oxygen in the Settling Column
(mg/l)

Station	Type A Init.	Range	Type B Init.	Range	Type C Init.	Range	Type D Init.	Range	Type E Init.	Range
#1--Silty Sand	6.6	3.4-4.0	---	---	---	---	0.5	nil	---	---
#2--Sandy Silt	6.54	0.4-1.4	0.4	0.0-0.5	7.2	1.9-2.7	0.56	nil	6.8	0.0-6.8
#3--Silty Sand	5.7-6.6	0.15-2.5	0.35	0.0-0.55	7.8	1.1-1.9	0.6	nil	7.3	0.05-7.3
#6--Silty Clay	6.2-7.0	0.0-0.48	0.4	nil	7.1	0.0-0.1	0.2	0.1-0.2	6.7	0.6-6.7
Morris Dam	2.3-6.6	0.8-2.3	0.2	0.1-0.2	---	---	---	---	---	---

A = untreated seawater

B = nitrogen prebubbled, quiescent

C = oxygen prebubbled, quiescent

D = continued bubbling with nitrogen

E = continued bubbling with compressed air

--not determined

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Table 40

Comparative Metal Release Factor

Individual element in seawater background = 1

Column Test Type	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
A	1.1	1.0	7.4	7.5	29.4	1.5	13.7	38.7	3.4	7.9
B	1.1	1.0	8.8	8.4	165.4	2.0	16.2	88.6	4.8	11.5
C	0.4	1.0	8.3	9.7	27.6	4.4	14.6	52.6	12.4	14.6
D	0.5	0.7	8.0	10.6	52.4	1.6	14.9	54.0	8.9	17.1
E	0.4	0.7	6.5	10.9	15.9	2.1	10.4	48.3	6.5	17.5
Ranges of seawater background, ppb	0.00–0.02	0.03–0.24	0.05–0.8	0.1–0.8	0.4–3.0	0.03–0.15	0.4–3.0	0.02–0.75	0.03–0.12	0.2–0.5

A = untreated seawater

B = nitrogen prebubbled, quiescent

C = oxygen prebubbled, quiescent

D = continued bubbling with nitrogen

E = continued bubbling with compressed air

Table 41

Changes in General Characteristics of Surface Sediments
(Top 1 cm) after Long-Term Incubation
(ppm dry sediment unless specified)

Parameter	Silty clay sediment (Sta.#6)				Silty sand sediment (Sta.#3)				Sandy silt (Sta. #2)	
	O	S	R	C	O	S	R	C	O	S
Dry weight, %	37.2	44.4	41.0	33.5	60.6	62.8	63.7	29.7	48.1	50.1
Total organic carbon, %	2.05	2.15	2.08	2.93	0.67	0.63	0.68	1.81	1.51	1.67
Total volatile solids, %	9.54	9.58	9.36	11.67	2.80	2.56	2.95	9.53	4.69	4.28
Immediate oxygen demand	658	1319	1825	3600	161	434	644	1291	495	623
Acid soluble sulfide	30	709	1021	2630	4	14	55	18	5	16
Organic nitrogen	2909	2819	2820	3002	647	580	615	1412	362	378
Total nitrogen	2909	2819	2820	3002	647	580	615	1412	362	378
Total phosphorus	1380	1410	1350	2750	620	663	615	1490	876	898

O = oxidizing condition
R = reducing condition
S = slightly oxidizing condition
C = resettled test

Table 42

Partitioning of Cadmium among Geochemical Fractions
after Long-Term Incubation
(percent total trace metal)

| Sediment sample | Authigenic fraction (marine derived) | | | | | | | Litho-genic fraction |
| | Non-nodular hydrogenous fraction | | | | Biogenic fraction | Nodular hydrogenous fraction | Total (including interstitial water) | |
	Soluble	Exchangeable	HAC Extractable	Total	Organic & sulfide	Reducible		
Silty clay (Sta. #6)								
I	trace	trace	3.52	3.52	37.37	45.01	85.90	14.10
O	0.07	trace	78.68	78.75	5.66	12.40	96.80	3.20
S	trace	trace	55.29	55.29	20.59	20.88	96.77	3.23
R	trace	trace	55.12	55.12	24.39	18.14	97.71	2.29
C	trace	trace	67.74	67.74	11.29	19.26	98.23	1.87
Silty sand (Sta. #3)								
I	trace	trace	42.64	42.64	15.83	32.94	91.50	8.50
O	trace	trace	88.24	88.24	trace	7.06	94.90	5.10
S	trace	trace	82.09	82.09	trace	23.99	94.78	5.22
R	trace	trace	83.62	83.62	trace	12.06	96.03	3.97
C	trace	trace	66.67	66.67	11.30	19.83	97.97	2.03
Sandy silt (Sta. #2)								
I	trace	trace	8.00	8.00	25.35	64.16	97.50	2.50
O	trace	trace	87.65	87.65	trace	9.64	97.06	2.94
S	trace	trace	87.92	87.92	trace	9.86	97.37	2.63

I = original sediment   O = oxidizing condition   S = slightly oxidizing condition
R = reducing condition   C = resettled test

Table 43

Partitioning of Chromium among Geochemical Fractions
after Long-Term Incubation
(percent total trace metal)

| Sediment sample | Authigenic fraction (marine derived) | | | | Biogenic fraction Organic & sulfide | Nodular hydrogenous fraction Reducible | Total (including interstitial water) | Lithogenic fraction |
| | Non-nodular hydrogenous fraction | | | | | | | |
	Soluble	Exchangeable	HAc Extractable	Total				
Silty clay (Sta. #6)								
I	0.006	0.004	2.82	2.83	—	—	—	—
O	trace	0.025	3.77	3.795	21.74	7.88	33.42	66.58
S	trace	0.018	1.79	1.808	24.40	5.23	31.45	68.55
R	trace	0.021	1.73	1.751	24.34	5.17	31.26	68.74
C	trace	0.018	1.96	1.978	38.88	5.29	46.16	53.86
Silty sand (Sta. #3)								
I	0.005	0.006	4.13	4.14	—	—	—	—
O	trace	0.030	8.00	8.03	29.81	8.18	46.03	53.97
S	trace	0.020	5.94	5.96	30.87	7.94	44.77	55.23
R	trace	0.019	3.78	3.80	34.41	8.07	46.28	53.72
C	trace	0.021	2.72	2.74	36.19	9.12	48.05	51.95
Sandy silt (Sta. #2)								
I	0.006	0.009	6.52	6.54	—	—	—	—
O	trace	0.028	8.19	8.218	23.01	10.73	41.96	58.04
S	trace	0.023	7.58	7.603	28.25	8.96	44.82	55.18

I = original sediment   O = oxidizing condition   S = slightly oxidizing condition
R = reducing condition   C = resettled test

Table 44

Partitioning of Copper among Geochemical Fractions
after Long-Term Incubation
(percent total trace metal)

Sediment sample	Authigenic fraction				Biogenic fraction Organic & sulfide	Nodular hydrogenous fraction Reducible	Total (including interstitial water)	Lithogenic fraction
	Non-nodular hydrogenous fraction							
	Soluble	Exchangeable	Extractable IAC	Total				
Silty clay (Sta. #6)								
I	trace	trace	0.006	0.006	--	--	--	--
O	0.028	0.163	19.39	19.58	49.04	13.36	81.98	18.02
S	0.008	0.003	10.31	10.32	55.99	8.38	74.69	25.31
R	trace	trace	4.52	4.52	65.09	10.18	79.79	20.21
C	trace	trace	4.45	4.45	59.78	11.93	76.16	23.84
Silty sand (Sta. #3)								
I	trace	trace	4.89	4.89	--	--	--	--
O	0.17	0.82	29.75	30.74	10.73	32.20	83.69	16.31
S	0.007	0.073	21.70	21.78	33.80	25.94	81.54	18.46
R	trace	trace	19.14	19.14	39.53	22.43	81.11	18.89
C	0.022	0.032	18.02	18.07	40.72	15.92	74.72	25.28
Sandy silt (Sta. #2)								
I	trace	trace	0.045	0.046	--	--	--	--
O	0.012	0.164	23.31	23.49	39.62	18.96	82.07	17.93
S	0.002	0.058	19.55	19.61	39.72	18.99	78.33	21.67

I = original sediment   O = oxidizing condition   S = slightly oxidizing condition
R = reducing condition   C = resettled test

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Table 45

Partitioning of Iron among Geochemical Fractions
after Long-Term Incubation
(percent total trace metal)

Sediment sample	Authigenic fraction				Biogenic fraction Organic & sulfide	Nodular hydrogenous fraction Reducible	Total (including inter-stitial water)	Litho-genic fraction
	Non-nodular hydrogenous fraction							
	Soluble	Exchangeable	HAC Extractable	Total				
Silty clay (Sta. #6)								
I	0.16	trace	12.46	12.62	--	--	25.40	74.60
O	trace	trace	8.04	8.04	13.36	9.80	31.20	68.80
S	trace	trace	4.21	4.21	17.70	4.44	26.35	73.65
R	trace	trace	4.53	4.53	23.39	4.97	32.89	67.11
C	trace	trace	4.96	4.96	22.13	5.25	32.34	67.66
Silty sand (Sta. #3)								
I	0.120	trace	5.83	5.95	--	--	19.90	80.10
O	trace	trace	12.08	12.08	9.82	11.98	33.88	66.12
S	trace	trace	6.32	6.32	11.29	6.24	23.85	76.15
R	trace	trace	5.41	5.41	11.66	5.60	22.68	77.32
C	trace	trace	4.56	4.56	18.87	8.40	31.84	68.16
Sandy silt (Sta. #2)								
I	0.085	trace	8.48	8.56	--	--	22.67	77.33
O	trace	trace	8.47	8.47	19.15	10.75	38.39	61.61
S	trace	trace	7.12	7.12	16.89	9.73	33.75	66.25

I = original sediment   O = oxidizing condition   S = slightly oxidizing condition
R = reducing condition   C = resettled test

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Table 48

Partitioning of Lead among Geochemical Fractions
after Long-Term Incubation
(percent total trace metal)

Sediment sample	Authigenic fraction				Biogenic fraction Organic & sulfide	Nodular hydrogenous fraction Reducible	Total (including interstitial water)	Lithogenic fraction
	Non-nodular hydrogenous fraction							
	Soluble	Exchangeable	HAC Extractable	Total				
Silty clay (Sta. #6)								
I	0.002	trace	0.30	0.30	--	--	--	--
O	0.001	trace	10.89	10.89	5.08	60.03	76.02	23.98
S	0.001	trace	10.50	10.50	7.15	57.14	74.85	25.20
R	0.002	trace	7.40	7.40	17.55	50.49	78.53	21.47
C	0.001	trace	13.95	13.95	27.71	51.55	93.22	6.78
Silty sand (Sta. #3)								
I	0.02	trace	16.58	16.60	--	--	--	--
O	trace	trace	12.84	12.84	6.24	60.09	79.42	20.58
S	trace	trace	14.81	14.81	3.94	62.08	80.85	19.15
R	0.001	trace	16.28	16.28	7.63	53.65	75.80	24.20
C	0.001	trace	5.51	5.51	26.05	35.94	67.53	32.47
Sandy silt (Sta. #2)								
I	trace	trace	10.08	10.08	--	--	--	--
O	0.001	trace	8.48	8.48	8.75	63.00	80.24	19.76
S	trace	trace	8.00	8.00	13.61	58.16	79.80	20.20

I = original sediment   O = oxidizing condition   S = slightly oxidizing condition
R = reducing condition   C = resettled test

Table 49

Partitioning of Zinc among Geochemical Fractions
after Long-Term Incubation
(percent total trace metal)

Sediment sample	Authigenic fraction				Biogenic fraction	Nodular hydrogenous fraction	Total (including interstitial water)	Lithogenic fraction
	Non-nodular hydrogenous fraction				Organic & sulfide	Reducible		
	Soluble	Exchangeable	HAC Extractable	Total				
Silty clay (Sta. #6)								
I	0.010	0.001	7.92	7.93	--	--	--	--
O	0.005	2.42	49.69	52.12	15.66	14.80	82.60	17.40
S	trace	0.151	37.72	37.87	24.89	22.15	84.93	15.07
R	0.007	0.138	35.96	36.11	28.51	25.76	90.41	9.59
C	0.003	0.109	41.70	41.81	25.81	23.11	90.74	9.26
Silty sand (Sta. #3)								
I	0.036	0.12	24.00	24.15	--	--	--	--
O	trace	1.46	44.53	45.99	10.76	16.01	72.79	27.21
S	trace	0.975	44.01	44.99	18.60	14.06	77.67	22.33
R	trace	0.408	38.70	39.11	17.99	15.83	72.94	27.06
C	0.003	0.385	41.81	42.20	20.58	18.92	81.72	18.28
Sandy silt (Sta. #2)								
I	0.024	0.005	19.12	19.15	--	--	--	--
O	trace	1.94	33.28	35.22	25.31	17.88	78.43	21.57
S	trace	0.981	44.27	44.25	21.36	12.94	79.59	20.41

I = original sediment   O = oxidizing condition   S = slightly oxidizing condition
R = reducing condition   C = resettled test

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Table 50

Composition of Interfacial Seawater after Long-Term Exposure
To Different Redox Conditions

Station/ Condition	Contact Time, days	pH	Acid Neutralizing Capacity, eq/l	Total Dissolved Carbonate, M	HCO_3^-, M	$CO_3^=$, M	Total Dissolved Phosphorus, M	Total Dissolved Nitrogen, ppm	Total Dissolved Silica, M	Total Dissolved Sulfide, M	NH_3-N, M	R_1^*	R_2^*	R_3^*	R_4^*	R_5^*	R_6^*	R_7^*	R_8^*
3 Oxidizing	150	7.35	14.17×10^{-3}	1.47×10^{-2}	1.38×10^{-2}	1.62×10^{-4}	1.61×10^{-6}	0.47	3.21×10^{-4}	0.00	0.00	3.09×10^{-10}	0.00	0.00	1.73×10^{2}	5.59×10^{11}	1.94×10^{3}	6.26×10^{12}	1.48×10^{3}
3 Reducing	150	6.98	8.10×10^{-3}	8.44×10^{-3}	7.46×10^{-3}	3.74×10^{-5}	1.10×10^{-5}	6.25	6.07×10^{-4}	4.53×10^{-4}	1.07×10^{-4}	2.44×10^{-10}	7.57×10^{-7}	3.14×10^{3}	7.49×10^{2}	3.07×10^{12}	8.39×10^{3}	3.44×10^{13}	1.60×10^{3}
3 Resettled Test	150	7.30	7.28×10^{-3}	7.63×10^{-3}	7.13×10^{-3}	7.46×10^{-5}	3.23×10^{-6}	0.40	6.54×10^{-4}	0.00	0.00	5.34×10^{-10}	0.00	0.00	3.75×10^{2}	7.03×10^{11}	4.20×10^{3}	7.88×10^{12}	1.23×10^{3}
6 Oxidizing	150	7.37	19.57×10^{-3}	2.03×10^{-2}	1.91×10^{-2}	2.35×10^{-4}	1.94×10^{-6}	0.00	4.93×10^{-4}	0.00	0.00	2.34×10^{-10}	0.00	0.00	1.19×10^{2}	5.10×10^{11}	1.33×10^{3}	5.71×10^{12}	1.62×10^{3}
6 Slightly Oxidizing	150	7.00	11.76×10^{-3}	1.22×10^{-2}	1.08×10^{-2}	5.69×10^{-5}	2.58×10^{-5}	20.00	6.25×10^{-4}	2.50×10^{-6}	7.14×10^{-4}	1.76×10^{-10}	2.97×10^{-9}	1.69×10^{-8}	4.92×10^{2}	2.80×10^{12}	5.51×10^{3}	3.14×10^{13}	1.79×10^{3}
6 Reducing	150	6.75	8.34×10^{-3}	8.46×10^{-3}	6.95×10^{-3}	2.06×10^{-5}	2.58×10^{-5}	13.26	4.82×10^{-4}	4.84×10^{-4}	8.57×10^{-4}	1.54×10^{-10}	7.09×10^{-7}	4.62×10^{3}	1.36×10^{3}	8.85×10^{12}	1.52×10^{4}	9.92×10^{13}	1.87×10^{3}
6 Resettled Test	150	7.85	19.19×10^{-3}	1.75×10^{-2}	1.66×10^{-2}	6.16×10^{-4}	2.58×10^{-5}	10.20	5.93×10^{-4}	7.81×10^{-4}	5.36×10^{-4}	8.14×10^{-10}	8.38×10^{-7}	1.03×10^{3}	4.55×10	5.59×10^{10}	5.09×10^{2}	6.26×10^{11}	1.07×10^{3}
2 Oxidizing	120	7.73	9.90×10^{-3}	9.83×10^{-3}	9.36×10^{-3}	2.63×10^{-4}	6.46×10^{-6}	0.93	3.57×10^{-4}	0.00	0.00	1.10×10^{-9}	0.00	0.00	1.06×10^{2}	9.70×10^{10}	1.19×10^{3}	1.09×10^{12}	9.70×10^{2}
2 Slightly Oxidizing	120	7.78	10.10×10^{-3}	9.98×10^{-3}	9.46×10^{-3}	3.00×10^{-4}	3.88×10^{-6}	0.95	4.55×10^{-4}	0.00	0.00	1.21×10^{-9}	0.00	0.00	9.33×10	7.71×10^{10}	1.05×10^{3}	8.64×10^{11}	9.38×10^{2}
2 Resettled Test	120	8.30	6.12×10^{-3}	5.58×10^{-3}	5.02×10^{-3}	5.26×10^{-4}	7.10×10^{-6}	0.10	2.68×10^{-4}	0.00	0.00	7.57×10^{-9}	0.00	0.00	5.32×10	7.03×10^{9}	5.96×10^{2}	7.88×10^{10}	5.09×10^{2}

$$R_1 = \frac{(SO_4^=)}{(CO_3^=)} \qquad R_2 = \frac{(S^=)}{(CO_3^=)} \qquad R_3 = \frac{(S^=)}{(OH^-)^2}$$

$$R_4 = \frac{(SO_4^=)}{(CO_3^=)} \qquad R_5 = \frac{(SO_4^=)}{(OH^-)^2} \qquad R_6 = \frac{(Cl^-)^2}{(CO_3^=)} \qquad R_7 = \frac{(Cl^-)^2}{(OH^-)^2}$$

$$R_8 = \left[\frac{(CO_3^=)}{[(OH^-)^2(CO_2^=)^2]} \right]^{1/3}$$

Assuming $(Cl^-) = 0.56M$, $(SO_4^=) = 0.028M$, $\Sigma B_D = 6$ ppm, $T = 10°C$. All K values for carbonate species from Stumm and Morgan (Ref. 42).

Table 51

Trace Metals Association with Total Organics, Humic Acid, and Fulvic Acid in Silty Sand Sediment (Sta. #1), Los Angeles Harbor

Element	Total trace metal conc. (mg/kg)	Trace metal in TO(NaOH)$_{sx}$* (mg/kg)	Trace metal with humic acid* (mg/kg)	Trace metal with fulvic acid* (mg/kg)	% trace metals assoc. with TO(NaOH)$_{sx}$	% trace metals assoc. with humic acid	% trace metals assoc. with fulvic acid
Ag	0.20	0.04	0.02	0.03	20.0	10.0	15.0
Al	11,360	121.1	86.4	32.5	1.06	0.76	0.28
As*	6.30	0.86	0.67	0.10	13.6	10.6	1.58
Cd*	0.51	0.02	0.01	0.006	3.91	1.95	1.17
Cr	50.6	1.00	0.61	0.32	1.96	1.21	0.63
Cu	21.5	0.82	0.36	0.45	3.81	1.67	2.09
Fe*	12,780	215.1	113.6	100.3	1.68	0.89	0.78
Mn*	334.1	0.37	0.21	0.13	0.11	0.063	0.039
Ni*	12.3	0.45	0.28	0.19	3.65	2.27	1.54
Pb*	4.24	0.06	0.03	0.028	1.41	0.71	0.66
V	53.1	1.81	0.83	0.92	3.40	1.56	1.73
Zn	66.6	2.60	1.80	0.70	3.90	2.70	1.05

*Total trace metal concentration obtained with simultaneous use of background corrector

TO(NaOH)$_{sx}$ represents total organic contents through successive extractions with sodium hydroxide

--not determined

Table 52

Trace Metals Association with Total Organics, Humic Acid, and Fulvic Acid in Sandy Silt Sediment (Sta. #2), Los Angeles Harbor

Element	Total trace metal conc. (mg/kg)	Trace metal in TO(NaOH)$_{sx}$ (mg/kg)	Trace metal with humic acid* (mg/kg)	Trace metal with fulvic acid* (mg/kg)	% trace metals assoc. with TO(NaOH)$_{sx}$	% trace metals assoc. with humic acid	% trace metals assoc. with fulvic acid
Ag	0.66	0.06	0.02	0.03	9.09	3.03	4.54
Al	13,370	93.3	46.5	43.4	0.69	0.34	0.32
As*	13.9	1.14	0.90	0.27	8.21	6.47	1.94
Cd*	1.77	0.04	0.02	0.015	2.25	1.13	0.85
Cr	121.4	1.80	0.85	0.93	1.48	0.70	0.76
Cu	93.8	1.12	0.83	0.36	1.19	0.88	0.38
Fe*	27,450	586.8	263.6	315.8	2.13	0.96	1.15
Mn*	455.6	0.26	0.12	0.19	0.057	0.026	0.04
Ni*	28.4	0.95	0.63	0.36	3.34	2.22	1.26
Pb*	13.1	0.13	0.06	0.06	0.99	0.46	0.46
V	81.9	6.31	4.28	2.23	7.70	5.22	2.72
Zn	180.1	5.10	2.80	2.40	2.83	1.55	1.33

*Trace metal concentration obtained with simultaneous use of background corrector

TO(NaOH)$_{sx}$ represents total organic contents through successive extractions with sodium hydroxide

—not determined

Table 53

Trace Metals Association with Total Organics, Humic Acid, And Fulvic Acid in Silty Sand Sediment (Sta. #3), Los Angeles Harbor

Element	Total trace metal conc. (mg/kg)	Trace metal in TO(NaOH)sx* (mg/kg)	Trace metal with humic acid* (mg/kg)	Trace metal with fulvic acid* (mg/kg)	% trace metals assoc. with TO(NaOH)sx	% trace metals assoc. with humic acid	% trace metals assoc. with fulvic acid
Ag	0.28	0.002	0.0006	0.001	0.71	0.35	0.21
Al	14,650	180.3	70.6	102.5	1.23	0.69	0.48
As*	9.05	0.38	0.23	0.18	4.19	1.98	2.54
Cd*	0.67	0.006	0.003	0.003	0.89	0.47	0.44
Cr	63.7	0.68	0.27	0.32	1.06	0.50	0.42
Cu	54.2	1.08	0.42	0.83	1.99	1.53	0.77
Fe*	19,620	335.6	156.3	195.3	1.71	0.99	0.84
Mn*	428.4	0.08	0.03	0.05	0.02	0.01	0.007
Ni*	21.4	0.82	0.45	0.38	3.83	1.77	2.10
Pb*	7.69	0.63	0.35	0.38	8.20	4.94	4.55
V	69.6	4.87	2.43	2.85	6.99	4.09	3.50
Zn	108.5	5.21	2.37	2.86	4.80	2.63	2.18

*Trace metal concentration obtained with simultaneous use of background corrector

TO(NaOH)$_{sx}$ represents total organic contents through successive extractions with sodium hydroxide

--not determined

Table 54

Trace Metals Association with Total Organics, Humic Acid,
and Fulvic Acid in Silty Sand Sediment (Sta. #4),
Los Angeles Harbor

Element	Total trace metal conc. (mg/kg)	Trace metal in TO(NaOH)$_{sx}$* (mg/kg)	Trace metal with humic acid* (mg/kg)	Trace metal with fulvic acid* (mg/kg)	% trace metals assoc. with TO(NaOH)$_{sx}$	% trace metals assoc. with humic acid	% trace metals assoc. with fulvic acid
Ag	0.18	0.003	0.002	0.002	1.68	1.12	1.12
Al	11,910	416.8	278.5	153.6	3.49	2.33	1.28
As*	8.21	0.35	0.18	0.19	4.26	2.19	2.31
Cd*	0.34	0.02	0.008	0.005	4.70	2.35	1.47
Cr	51.7	0.37	0.26	0.15	0.72	0.50	0.29
Cu	41.7	0.17	0.09	0.06	0.41	0.22	0.14
Fe*	20,380	305.7	183.5	124.5	1.49	0.90	0.61
Mn*	494.4	0.05	0.03	0.02	0.009	0.006	0.004
Ni*	19.5	0.59	0.33	0.26	3.00	1.69	1.34
Pb*	7.03	0.30	0.14	0.18	4.26	1.99	2.56
V	50.9	1.78	1.31	0.95	3.49	2.22	1.86
Zn	95.8	4.80	2.80	1.60	5.01	2.92	1.67

*Trace metal concentration obtained with simultaneous use of background corrector

TO(NaOH)$_{sx}$ represents total organic contents through successive extractions with sodium hydroxide

--not determined

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Table 55

Trace Metals Association with Total Organics, Humic Acid, and Fulvic Acid in Silty Sand Sediment (Sta. #5), Los Angeles Harbor

Element	Total trace metal conc. (mg/kg)	Trace metal in TO(NaOH)$_{sx}$* (mg/kg)	Trace metal with humic acid* (mg/kg)	Trace metal with fulvic acid* (mg/kg)	% trace metals assoc. with TO(NaOH)$_{sx}$	% trace metals assoc. with humic acid	% trace metals assoc. with fulvic acid
Ag	0.21	0.002	0.0009	0.0008	0.97	0.43	0.38
Al	22,200	215.4	110.7	108.5	0.97	0.49	0.48
As*	13.2	0.53	0.28	0.29	4.01	2.12	2.19
Cd*	0.33	0.005	0.003	0.003	1.51	0.91	0.76
Cr	64.4	1.15	0.83	0.62	1.78	1.28	0.96
Cu	56.1	1.08	0.87	0.38	1.92	1.55	0.67
Fe*	31,560	385.4	196.3	186.5	1.22	0.62	0.59
Mn*	667.4	0.78	0.54	0.36	0.11	0.08	0.05
Ni*	24.2	0.73	0.47	0.41	3.01	1.94	1.70
Pb*	13.9	0.15	0.08	0.09	1.07	0.57	0.65
V	84.4	1.10	0.83	0.38	1.30	0.98	0.45
Zn	137.2	5.63	3.62	2.13	4.10	2.64	1.55

*Trace metal concentration obtained with simultaneous use of background corrector.

TO(NaOH)$_{sx}$ represents total organic contents through successive extractions with sodium hydroxide

-- not determined

Table 56

Trace Metals Association with Total Organics, Humic Acid,
and Fulvic Acid in Silty Clay Sediment (Sta. #6),
Los Angeles Harbor

Element	Total trace metal conc. (mg/kg)	Trace metal in TO(NaOH)$_{sx}$* (mg/kg)	Trace metal with humic acid* (mg/kg)	Trace metal with fulvic acid* (mg/kg)	% trace metals assoc. with TO(NaOH)$_{sx}$	% trace metals assoc. with humic acid	% trace metals assoc. with fulvic acid
Ag	0.07	--	--	--	--	--	--
Al	10,370	105.5	58.5	61.3	1.01	0.56	0.59
As*	6.22	0.85	0.53	0.32	13.6	8.50	5.10
Cd*	0.18	0.008	0.004	0.003	4.44	2.22	1.66
Cr	58.5	0.45	0.26	0.25	0.77	0.44	0.43
Cu	557.7	9.51	5.41	3.83	1.70	0.97	0.68
Fe*	8,034	185.3	96.4	89.5	2.30	1.20	1.11
Mn*	336.5	0.41	0.21	0.19	0.12	0.062	0.056
Ni*	12.7	0.41	0.21	0.19	3.22	1.65	1.50
Pb*	122.3	1.50	0.81	0.63	1.22	0.66	0.52
V	43.3	1.32	0.81	0.36	3.05	1.87	0.83
Zn	212.0	6.81	3.85	2.89	3.21	1.82	1.36

*Trace metal concentration obtained with simultaneous use of background corrector.

TO(NaOH)$_{sx}$ represents total organic contents through successive extractions with sodium hydroxide

--not determined

Table 57

Trace Metals Association with Total Organics, Humic Acid, and Fulvic Acid in Sandy Silt Sediment (Sta. #7), Los Angeles Harbor

Element	Total trace metal conc. (mg/kg)	Trace metal in TO(NaOH)$_{sx}$* (mg/kg)	Trace metal with humic acid (mg/kg)	Trace metal with fulvic acid* (mg/kg)	% trace metals assoc. with TO(NaOH)$_{sx}$	% trace metals assoc. with humic acid	% trace metals assoc. with fulvic acid
Ag	0.18	0.02	0.01	0.006	--	5.55	3.33
Al	21,920	163.3	86.4	78.6	0.75	0.39	0.35
As*	5.18	0.27	0.14	0.15	5.21	2.70	2.89
Cd*	1.24	0.02	0.01	0.004	1.61	0.81	0.32
Cr	37.1	0.60	0.43	0.32	1.61	1.15	0.86
Cu	54.6	0.96	0.73	0.28	1.75	1.34	0.51
Fe*	17,210	346.5	165.5	188.8	2.01	0.96	1.09
Mn*	353.5	0.36	0.18	0.15	0.10	0.05	0.04
Ni*	17.5	0.68	0.48	0.21	3.88	2.74	1.20
Pb*	24.4	0.23	0.13	0.08	0.94	0.53	0.33
V	53.8	1.62	0.85	0.75	3.01	1.58	1.40
Zn	233.6	7.80	5.30	2.80	3.33	2.30	1.20

*Trace metal concentration obtained with simultaneous use of background corrector.

TO(NaOH)$_{sx}$ represents total organic contents through successive extractions with sodium hydroxide

--not determined

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Table 58

Organic Carbon Content of Los Angeles Harbor Sediments, Sodium Hydroxide-Extracted Organics, Humic Acid, and Fulvic Acid

Station	TOC_{sed} (%)	$TOC(NaOH)_{sx}$ (%)	TOC_{HA} (%)	TOC_{FA} (%)	$\dfrac{TOC(NaOH)_{sx}}{TOC_{sed}}$ (%)	$\dfrac{TOC_{HA}}{TOC_{sed}}$ (%)	$\dfrac{TOC_{FA}}{TOC_{sed}}$ (%)	$\dfrac{TOC_{HA}}{TOC(NaOH)_{sx}}$ (%)	$\dfrac{TOC_{FA}}{TOC(NaOH)_{sx}}$ (%)
1	0.379	0.213	0.019	0.125	56.2	5.01	32.9	8.92	58.6
2	0.797	0.389	0.229	0.195	48.8	28.7	24.4	58.8	50.1
3	0.497	0.365	0.098	0.222	73.4	19.7	44.6	26.8	60.8
4	0.277	0.225	0.060	0.113	81.2	21.6	40.8	26.6	50.2
5	0.857	0.335	0.120	0.158	39.0	14.0	18.4	35.8	47.1
6	0.343	0.107	0.011	0.039	31.2	3.20	11.4	10.2	36.4
7	1.661	1.800	0.920	0.536	118.1	55.4	32.3	51.1	29.7

TOC_{sed} represents total organic carbon content of total sediment

$TOC(NaOH)_{sx}$ represents total organic carbon content through successive extractions with NaOH

TOC_{HA} represents total organic carbon content of humic acid

TOC_{FA} represents total organic carbon content of fulvic acid

Table 59

Organic Carbon Contents of Los Angeles Harbor Sediments,
Sodium Hydroxide-Extracted Organics, Humic Acid, and Fulvic Acid

Station	Dry wt of sed. used for humic substance extract'n (grams)	Vol 0.1N NaOH used for humic substance extract'n (liters)	TOC_{sed} dry wt (%)	$TOC(NaOH)_{sx}$ mg/l	$TOC(NaOH)_{sx}$ dry wt (%)	TOC_{HA} mg/l	TOC_{HA} dry wt (%)	TOC_{FA} mg/l	TOC_{FA} dry wt (%)	$\dfrac{TOC(NaOH)_{sx}}{TOC_{sed}}$ (%)	$\dfrac{TOC_{HA}}{TOC_{sed}}$ (%)	$\dfrac{TOC_{FA}}{TOC_{sed}}$ (%)
1	155.4	5	0.51	41	0.132	6	0.019	36	0.116	25.9	3.7	22.7
2	109.0	5	1.43	110	0.505	50	0.229	77	0.353	35.3	16.0	24.7
3	132.8	5	0.83	77	0.290	26	0.098	47	0.177	34.9	11.8	21.3
4	142.2	5	0.65	64	0.225	17	0.060	41	0.144	34.6	9.2	22.2
5	132.8	5	0.87	64	0.241	32	0.120	37	0.139	27.7	13.8	16.0
6	162.0	2	0.45	41	0.051	9	0.011	32	0.040	11.3	2.4	8.9
7	127.2	3	1.71	490	1.156	390	0.920	270	0.637	67.6	53.8	37.3

TOC_{sed} represents total organic carbon content of total sediment

$TOC(NaOH)_{sx}$ represents total organic carbon content through successive extractions with NaOH

TOC_{HA} represents total organic carbon content of humic acid

TOC_{FA} represents total organic carbon content of fulvic acid

Table 60

Concentrations of Chlorinated Hydrocarbons
in Los Angeles Harbor Marine Sediments

Station	Moisture Content (%)	$\frac{p,p'DDE}{t-DDT}$ (%)	$\frac{o,p'DDE}{t-DDT}$ (%)	$\frac{p,p'DDD}{t-DDT}$ (%)	$\frac{o,p'DDD}{t-DDT}$ (%)	$\frac{p,p'DDT}{t-DDT}$ (%)	$\frac{o,p'DDT}{t-DDT}$ (%)	Total DDT (ppm)	Dieldrin (ppm)	Total PCB's (ppm)	Total Chlorinated Hydrocarbons (ppm)
1	22.3	71.0	6.3	10.6	6.0	2.8	3.2	0.321	0.9	0.046	0.368
2	45.5	69.6	7.1	10.0	5.2	5.0	3.1	3.212	1.3	0.285	3.498
3	33.6	65.9	9.1	10.8	6.4	3.1	4.6	0.831	0.9	0.123	0.955
4	28.9	68.6	8.2	10.2	6.2	2.8	4.0	0.353	0.6	0.05	0.403
5	33.6	62.0	8.4	14.5	3.4	7.7	4.0	0.297	2.2	0.071	0.370
6	19.0	61.7	8.7	12.2	7.8	7.0	2.6	0.115	2.1	0.190	0.307
7	36.4	60.7	6.1	16.6	6.1	6.5	4.0	0.247	4.5	0.214	0.466

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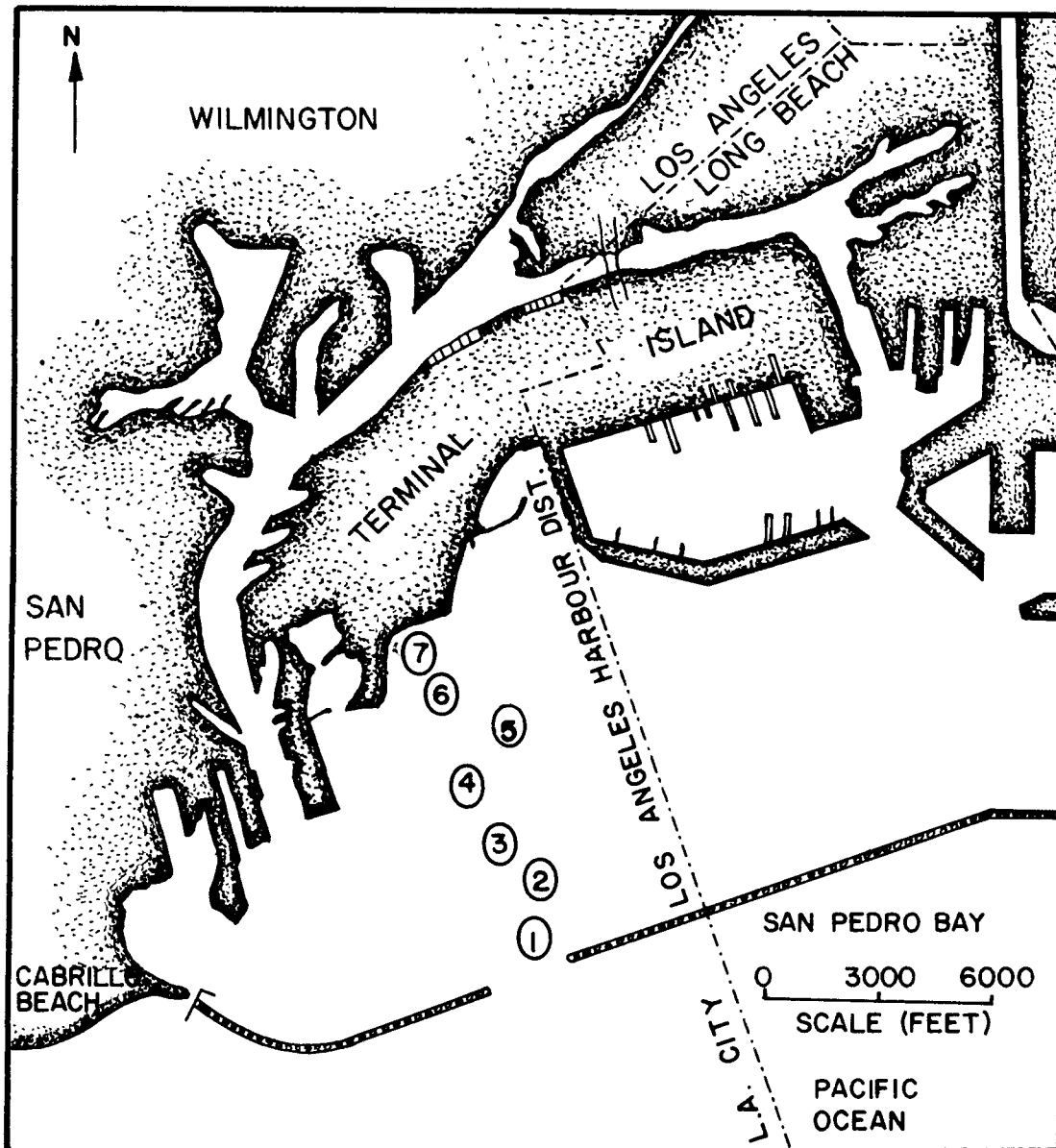
Figure 1.   Sampling stations for the proposed
liquefied natural gas route.
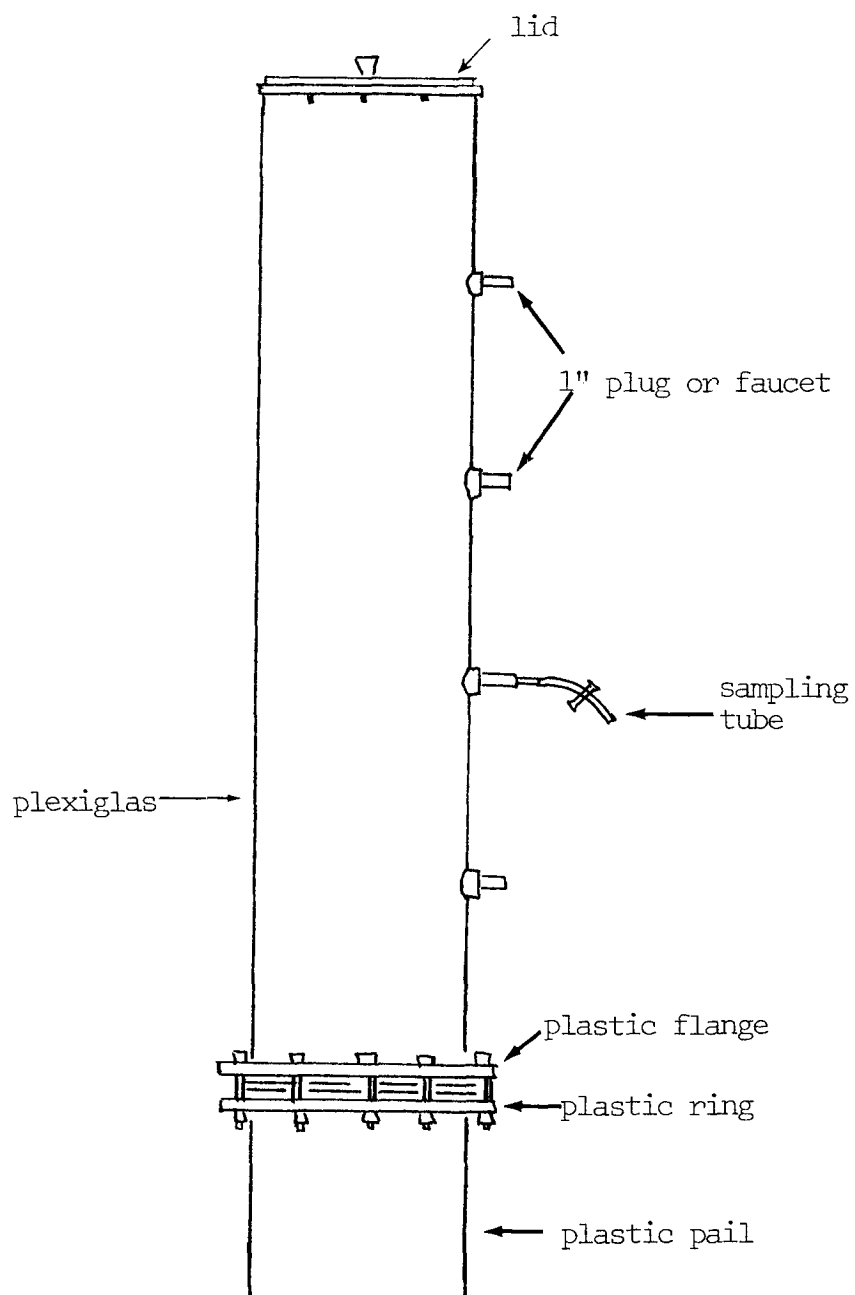
Figure 2. Schematic diagram of the settling column.

ORIGINAL SEAWATER
FILTER 0.05 μm
BUBBLE WITH DIFFERENT GASES

SEDIMENTS:
(1) SILTY CLAY TYPE
(2) SANDY SILT TYPE
(3) SILTY SAND TYPE

CONTACT AT SW:SED = 1:4

COLUMN TEST

SAMPLES FROM INTERFACIAL WATER

FILTER & ANALYZE

GENERAL PARAMETER: D.O., pH, ΣS_D

(1) TRACE METALS
(2) NUTRIENTS
(3) CHLORINATED HYDROCARBONS

LONG-TERM EXPERIMENTAL SETUP

GAS INLET

N_2

O_2 or Air or H_2S

20 L.

4 L.

1"

SEA WATER SAMPLING PORT

SEDIMENT

CONSTANT TEMP. DARK CHAMBER
(10 - 14°C)

Figure 3. Flow chart of long-term experiments on the transport
of trace metals between the sediment-seawater interface.

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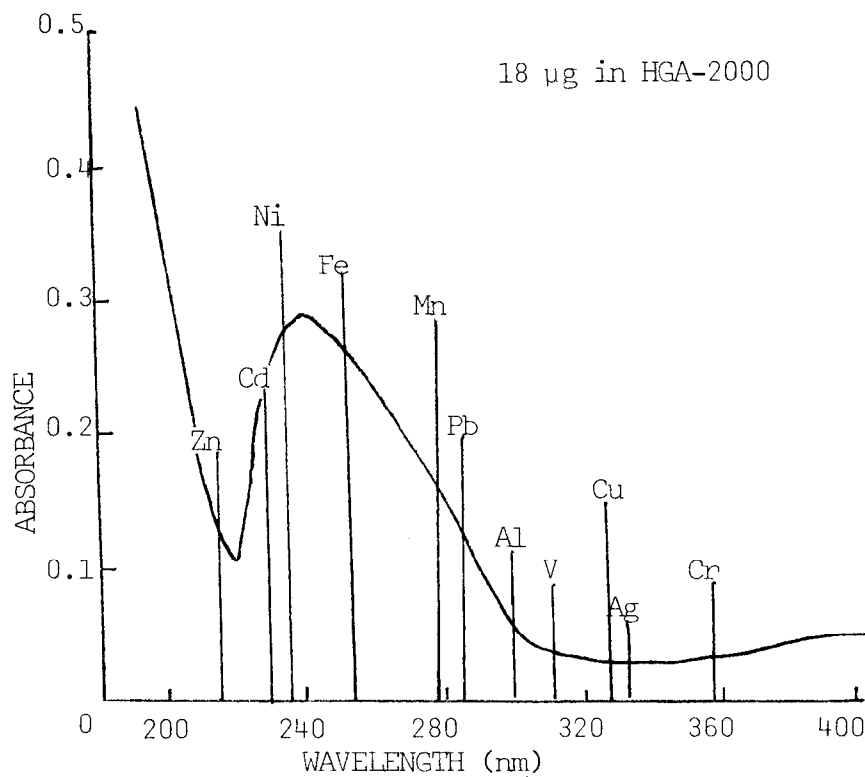
Figure 4. Sodium chloride molecular absorption spectrum.
          (after Reference No. 81)
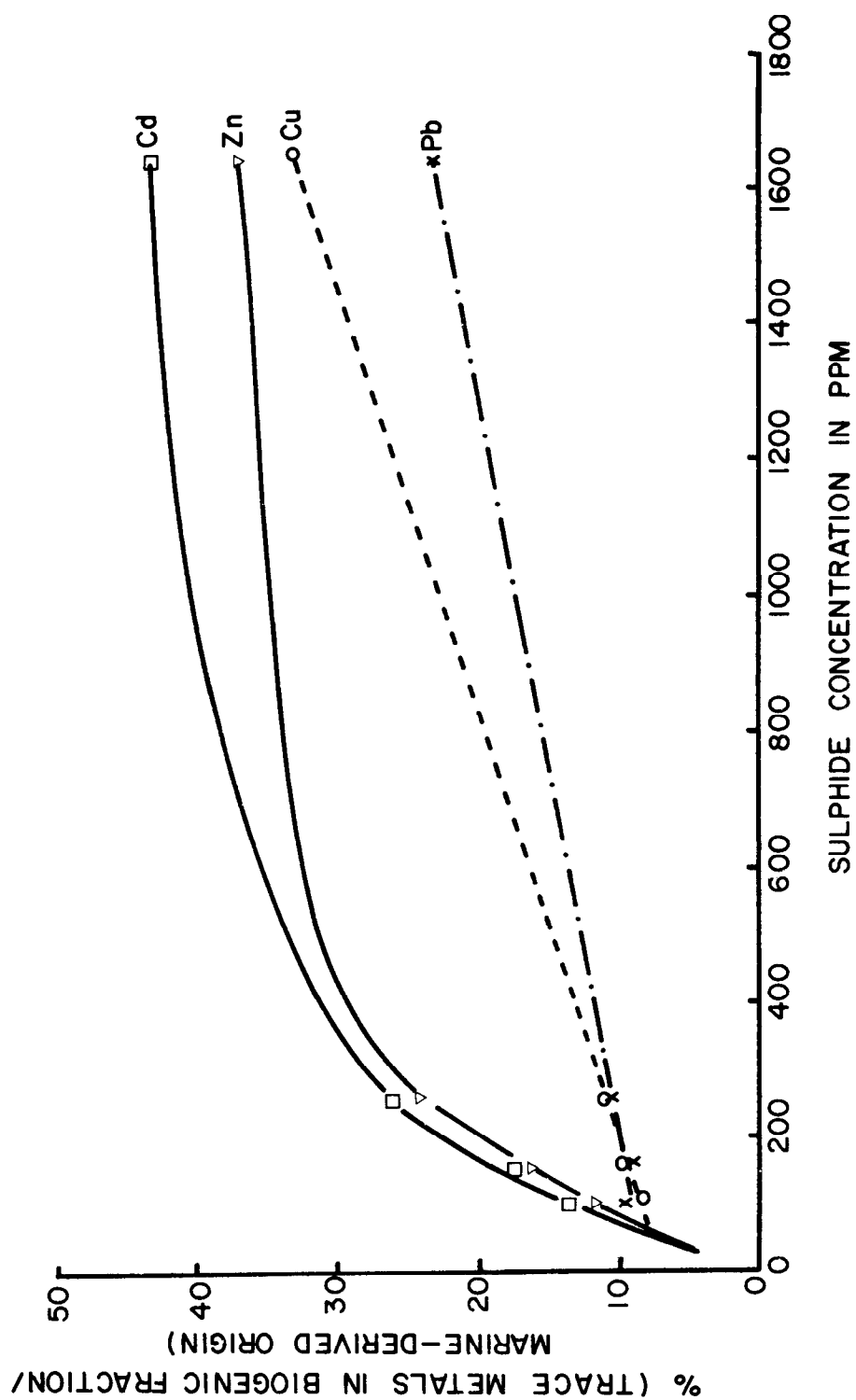
Figure 5. Relationship between sulfide concentration and trace metal associated with biogenic fraction.

183
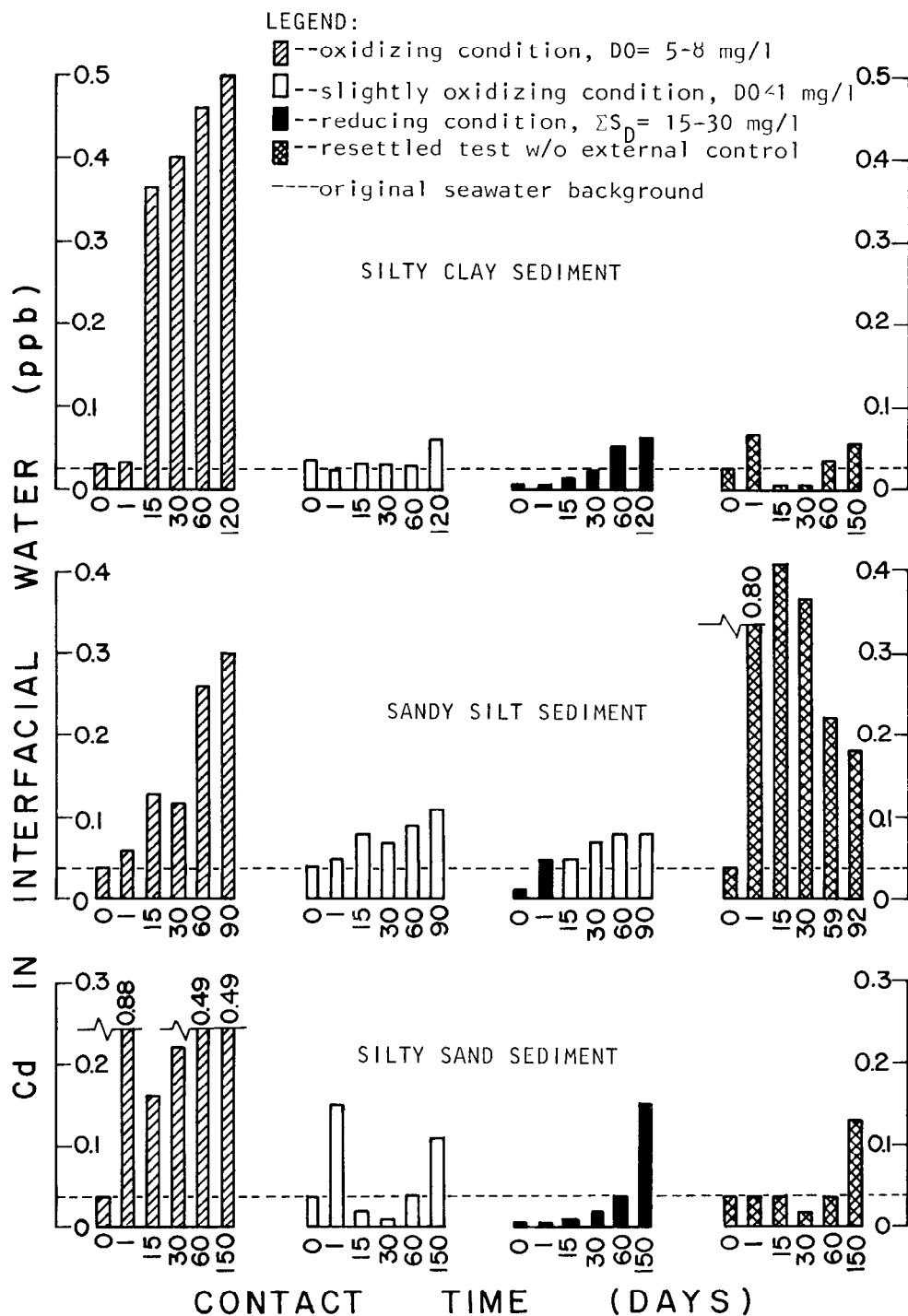
Figure 6. Transport of cadmium in sediment-seawater interfaces.
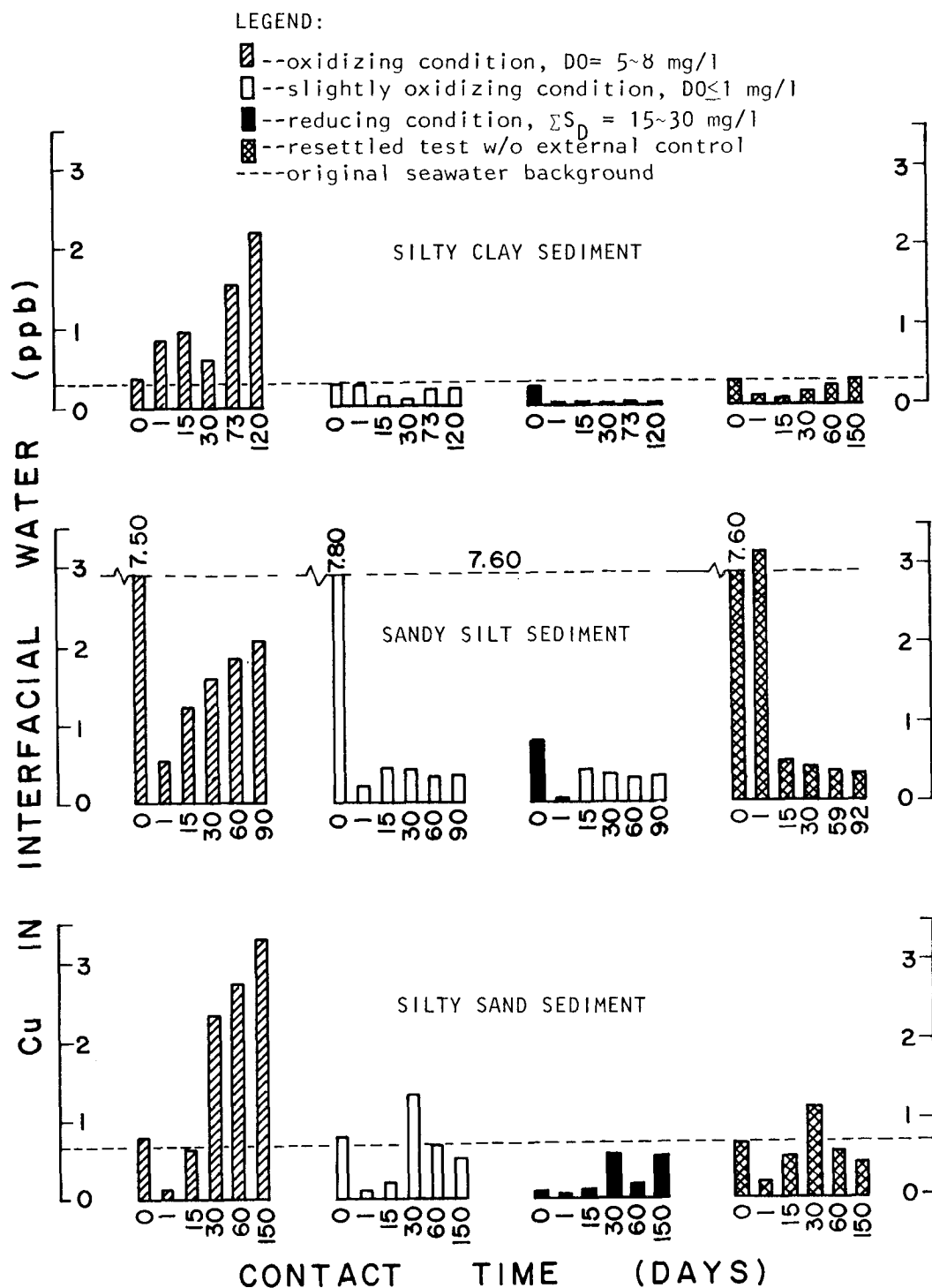
Figure 7. Transport of copper in sediment-seawater interfaces.

LEGEND:
▨ --oxidizing condition, DO=5∼8 mg/l
▯ --slightly oxidizing condition, DO≤1 mg/l
■ --reducing condition, ΣS$_D$=15∼30 mg/l
▧ --resettled test w/o external control
---- original seawater background

SILTY CLAY SEDIMENT

SANDY SILT SEDIMENT

SILTY SAND SEDIMENT

CONTACT   TIME   (DAYS)
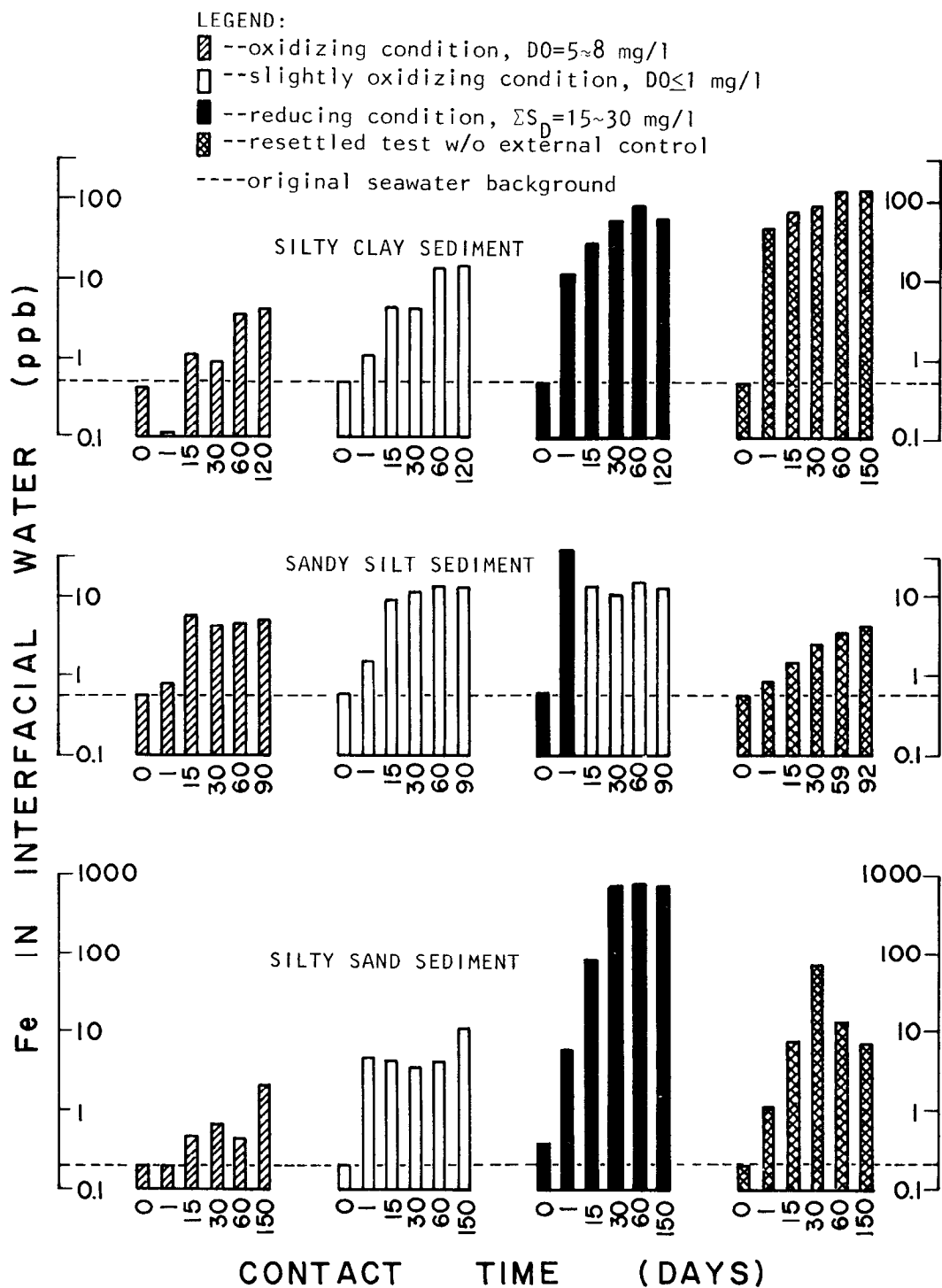
Figure 8.   Transport of iron in sediment-seawater interfaces.
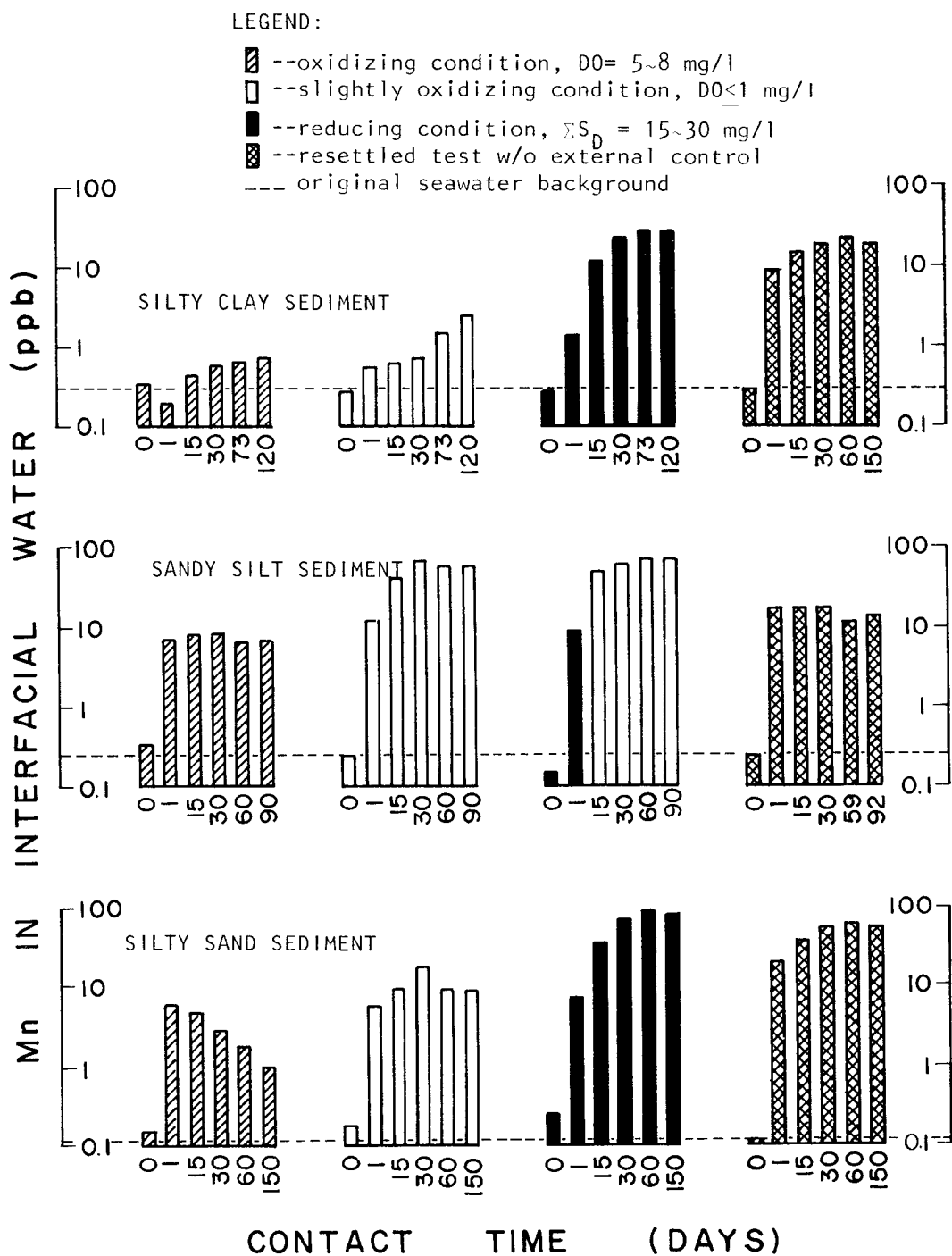
Figure 9.   Transport of manganese in sediment-seawater interfaces.
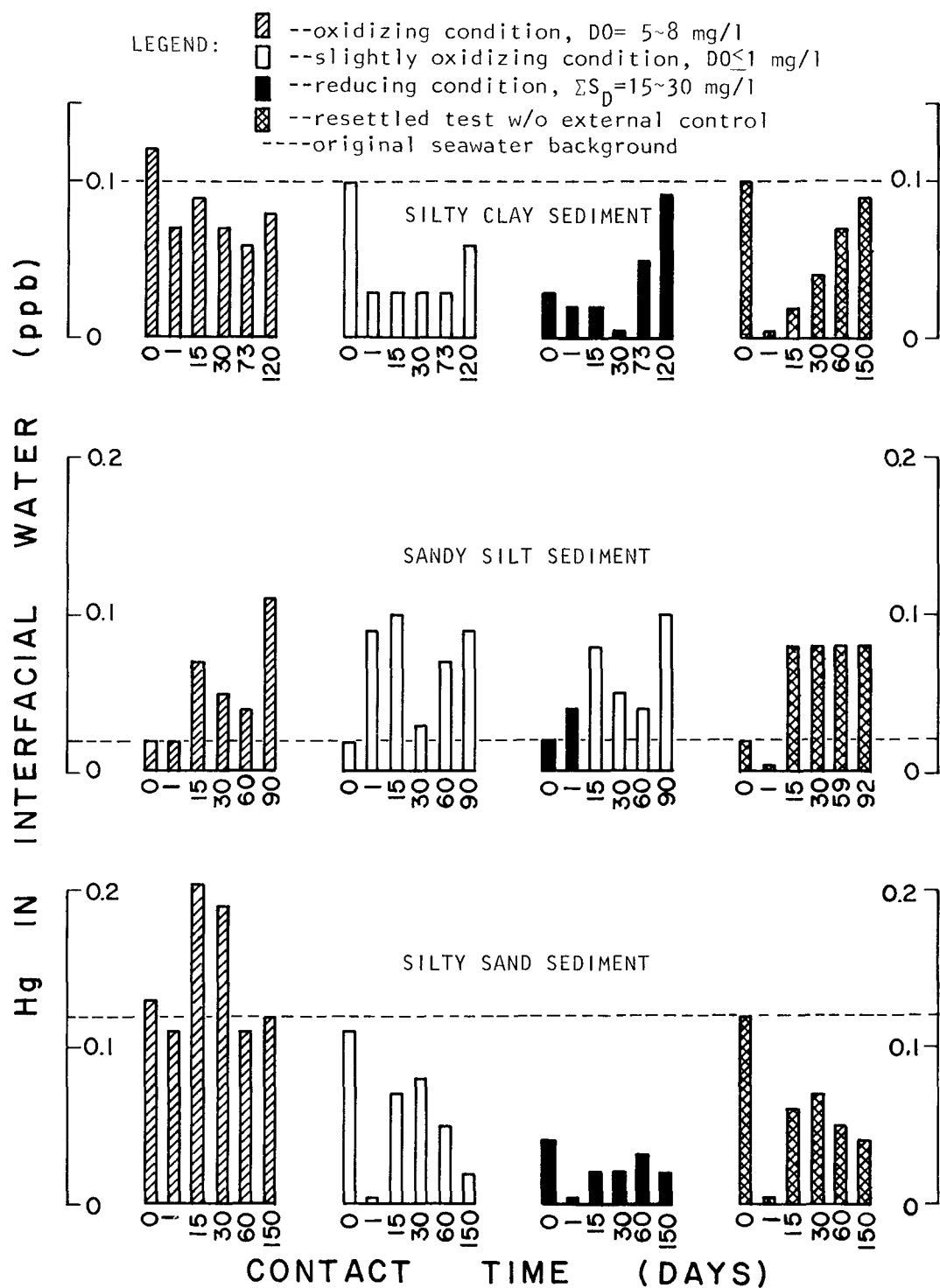
Figure 10. Transport of mercury in sediment-seawater interfaces.
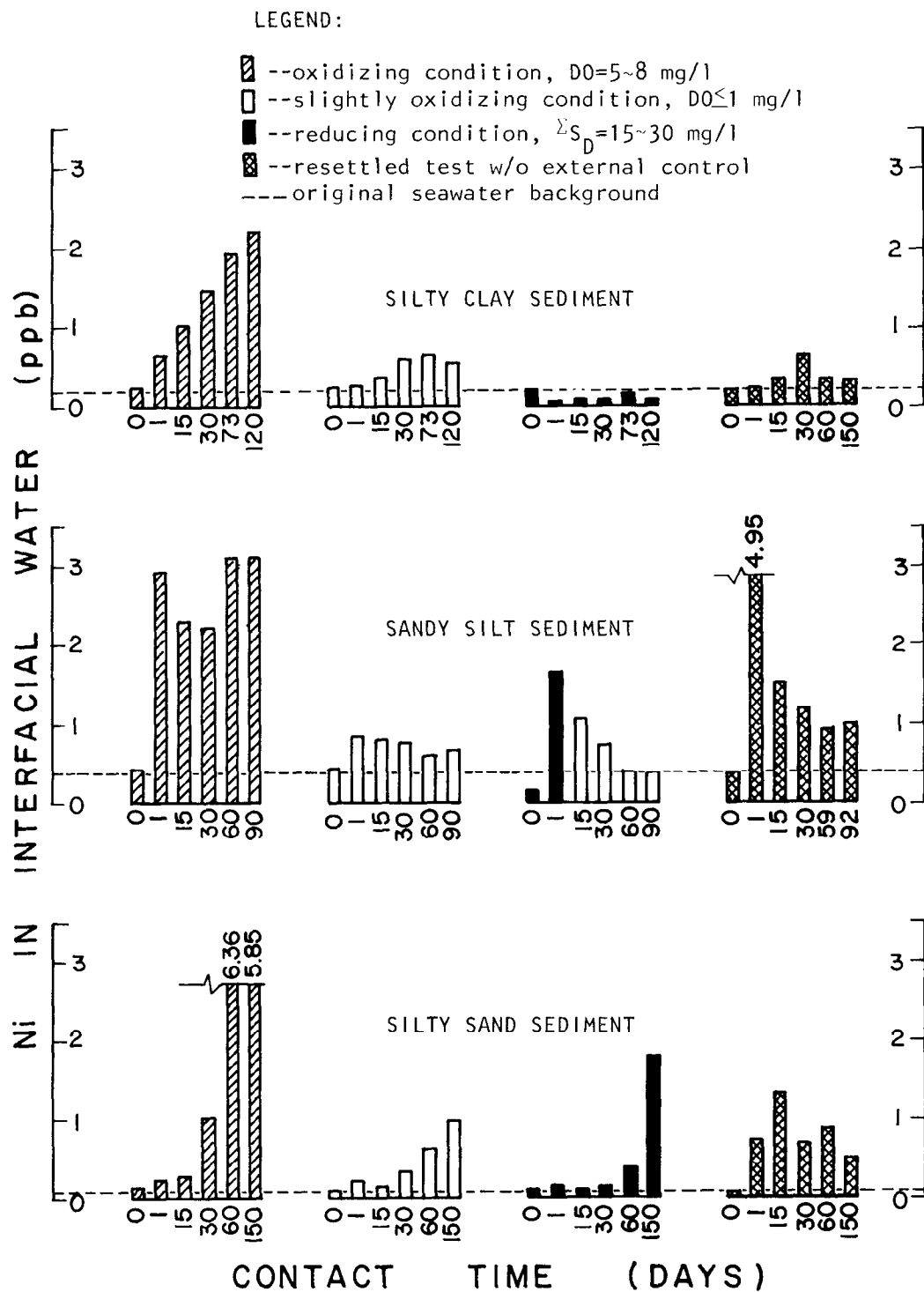
Figure 11. Transport of nickel in sediment-seawater interfaces.
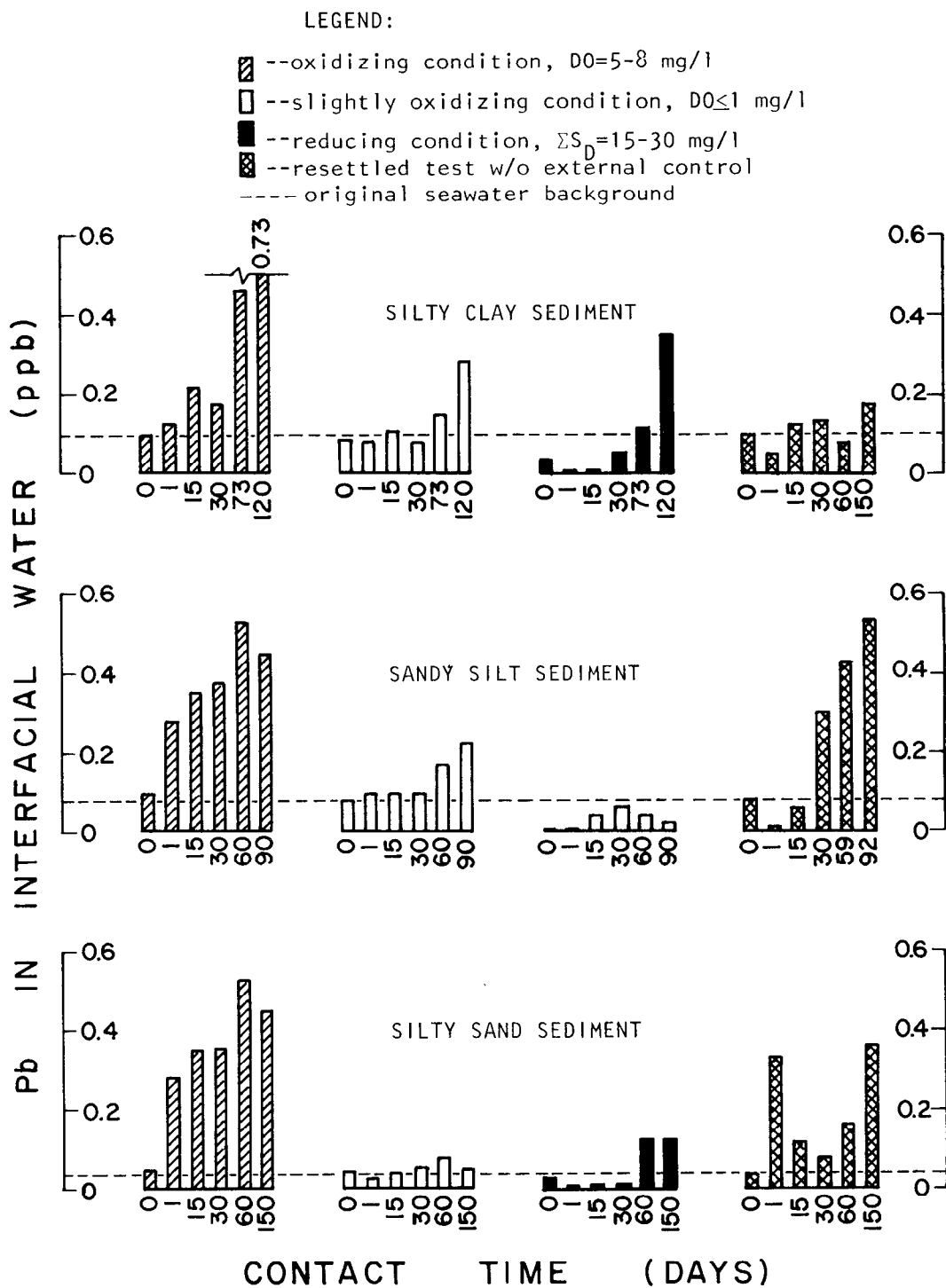
Figure 12.   Transport of lead in sediment-seawater interfaces.
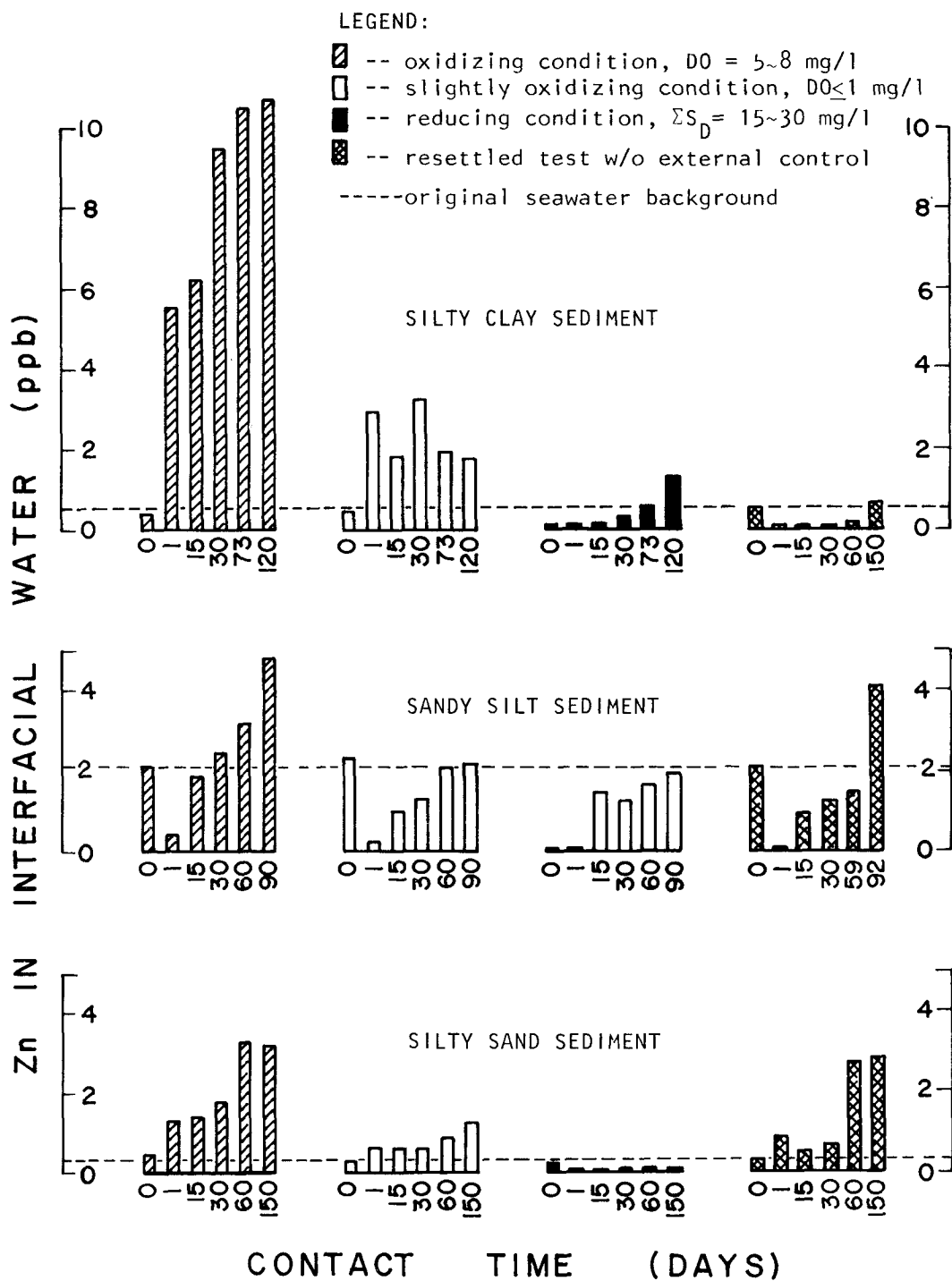
Figure 13. Transport of zinc in sediment-seawater interfaces.
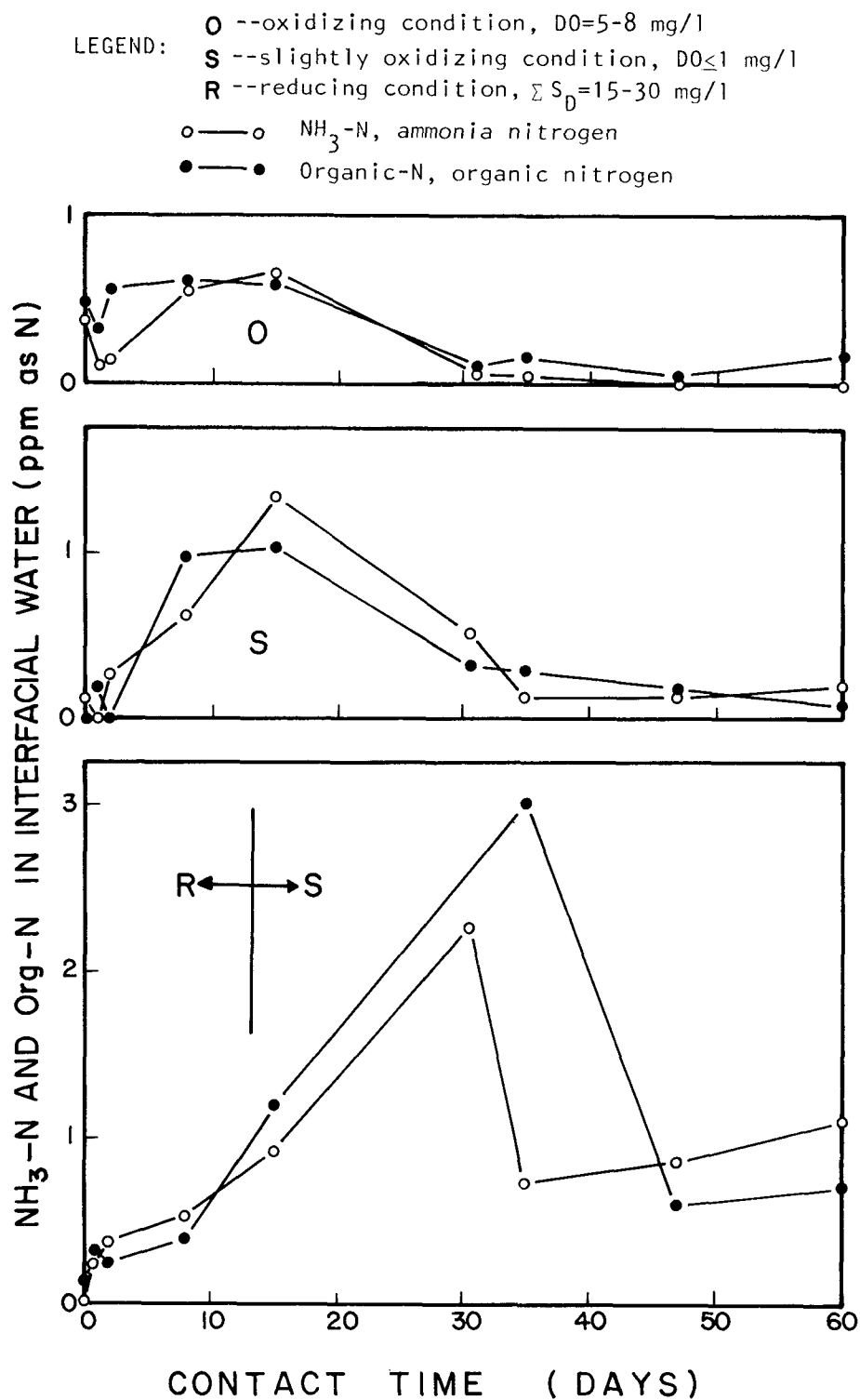
Figure 14.   Transport of ammonia nitrogen and organic
             nitrogen in sediment-seawater interfaces (sandy silt).

Figure 15. Transport of ammonia nitrogen and organic nitrogen in sediment-seawater interfaces (silty sand).

O --oxidizing condition, DO=5-8 mg/l
S --slightly oxidizing condition, DO$\leq$1 mg/l
R --reducing condition, ΣS_D=15-30 mg/l

o——o NH$_3$-N, ammonia nitrogen

•——• Organic-N, organic nitrogen
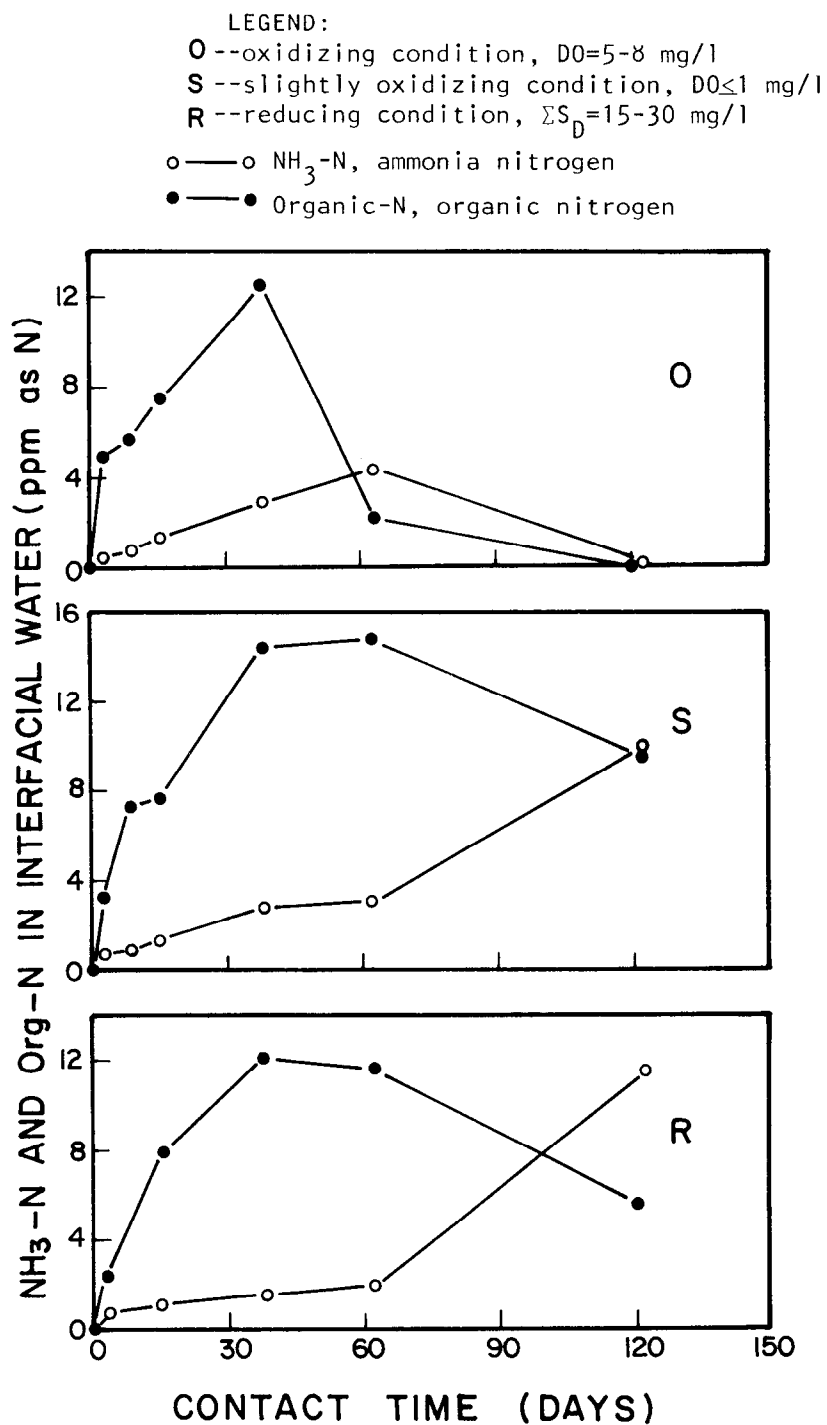
Figure 16. Transport of ammonia nitrogen and organic nitrogen in sediment-seawater interfaces (silty clay).

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LEGEND:

O --oxidizing condition, DO=5-8 mg/l

S --slightly oxidizing condition, DO≤1 mg/l

R --reducing condition, ΣS_D=15-30 mg/l

o———o NO_2-N (nitrite)

●———● NO_3-N (nitrate)
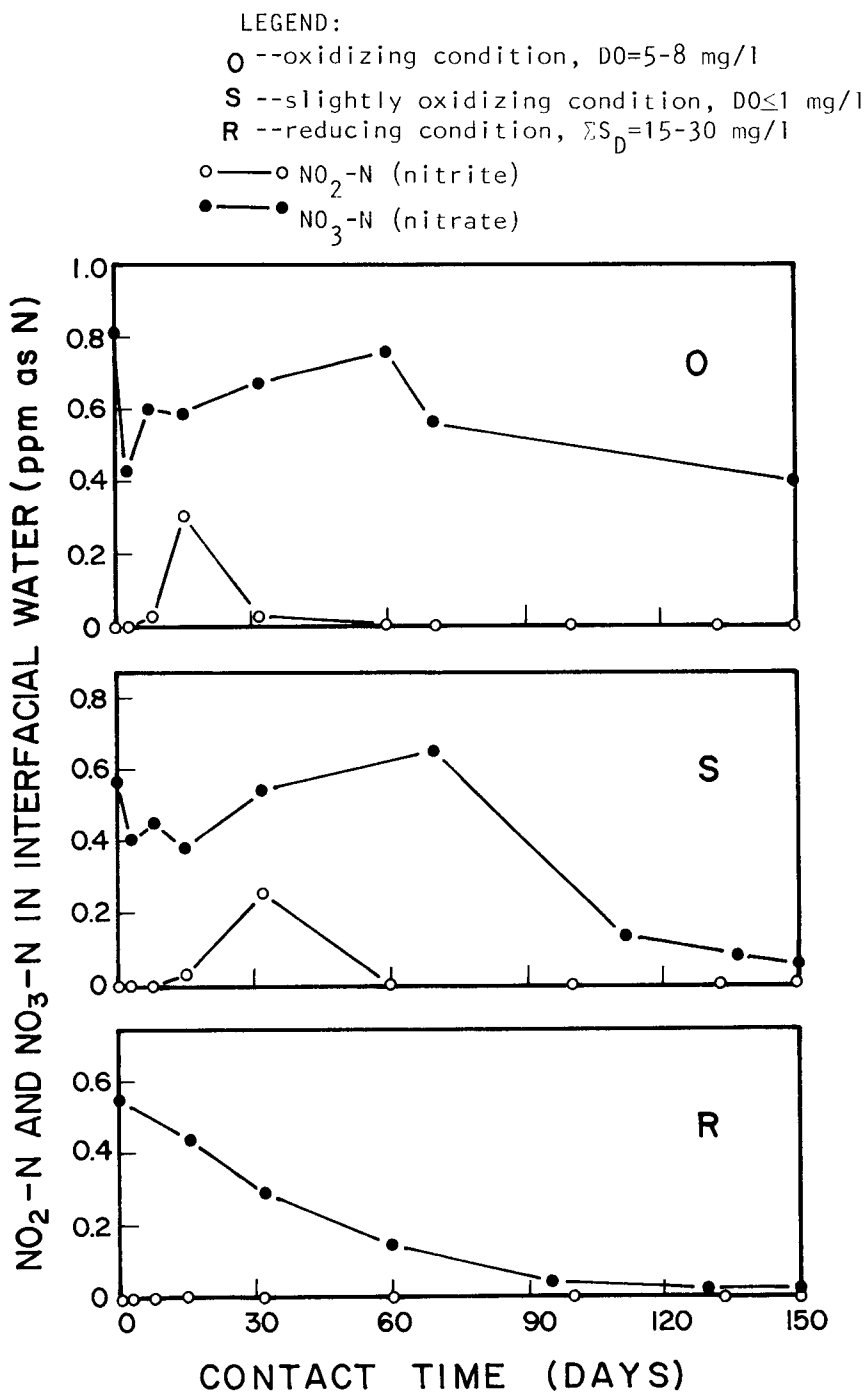
Figure 17. Transport of nitrite and nitrate in sediment-seawater interfaces (silty sand).

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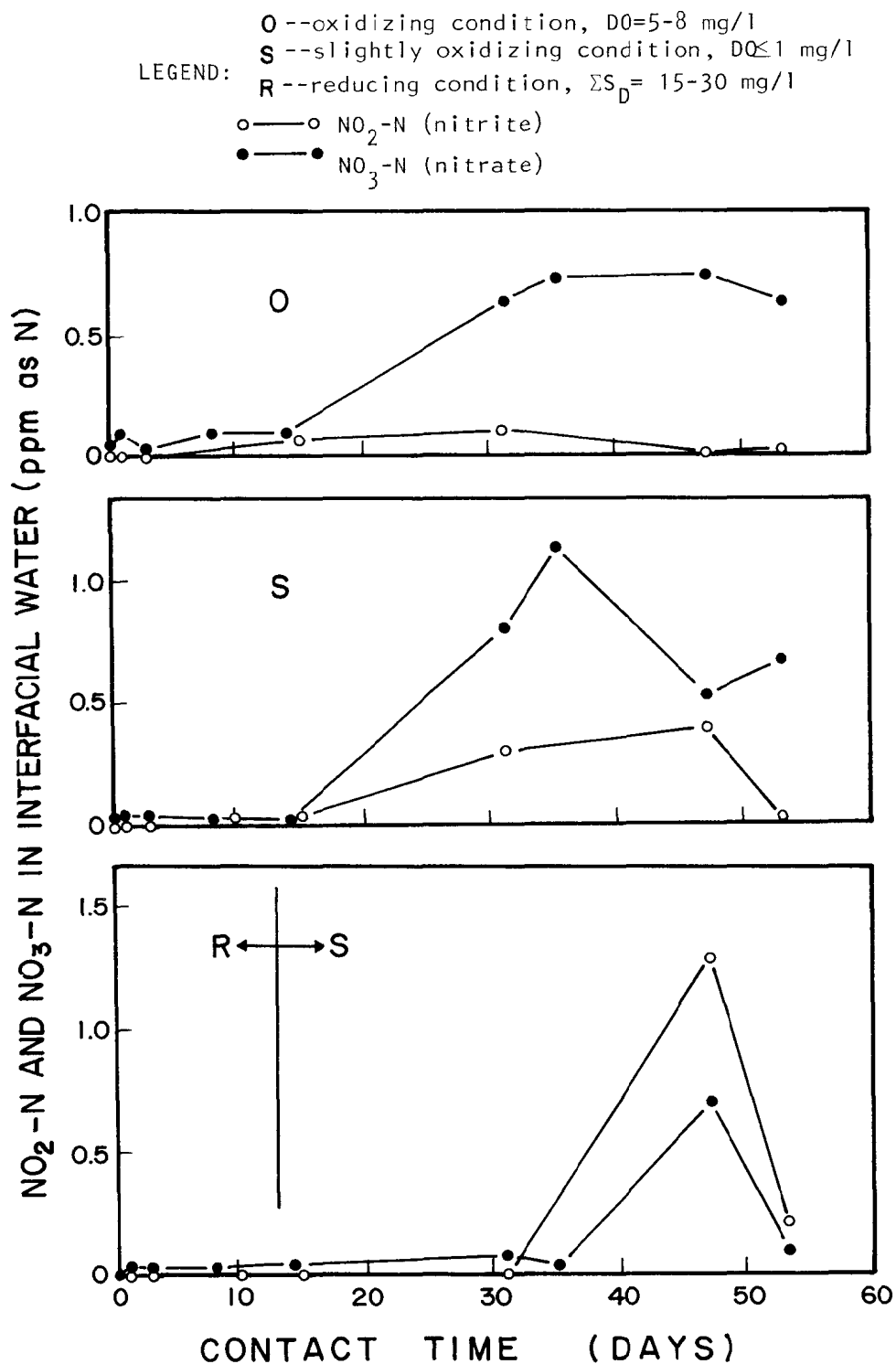
Figure 18. Transport of nitrite and nitrate in sediment-
seawater interfaces (sandy silt).
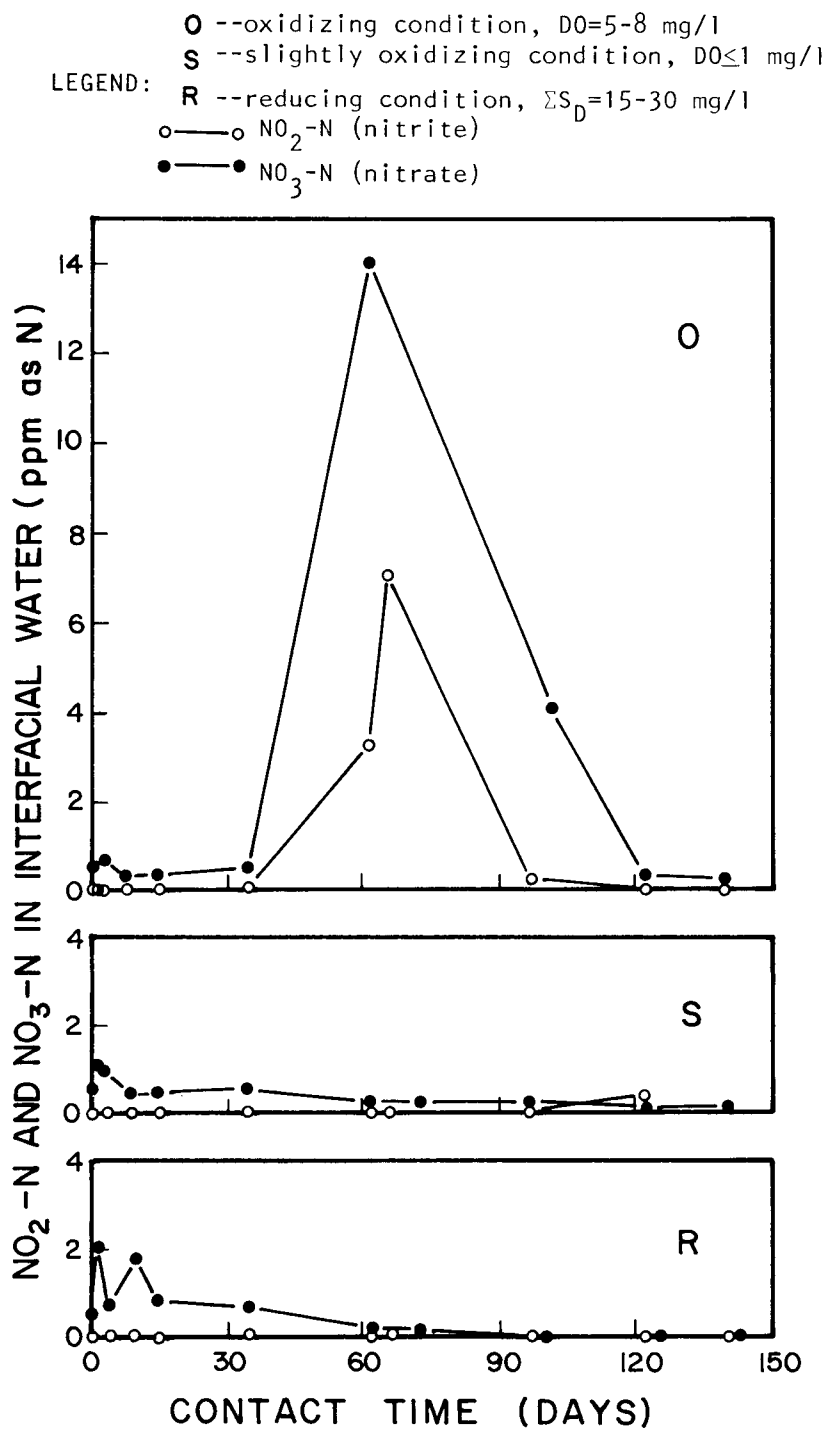
Figure 19. Transport of nitrite and nitrate in sediment-seawater interfaces (silty clay).

LEGEND:

O --oxidizing condition, DO=5-8 mg/l
S --slightly oxidizing condition, DO≤1 mg/l
R --reducing condition, ΣS_D = 15-30 mg/l

o——o total phosphorus
●——● orthophosphate
□——□ dissolved silica
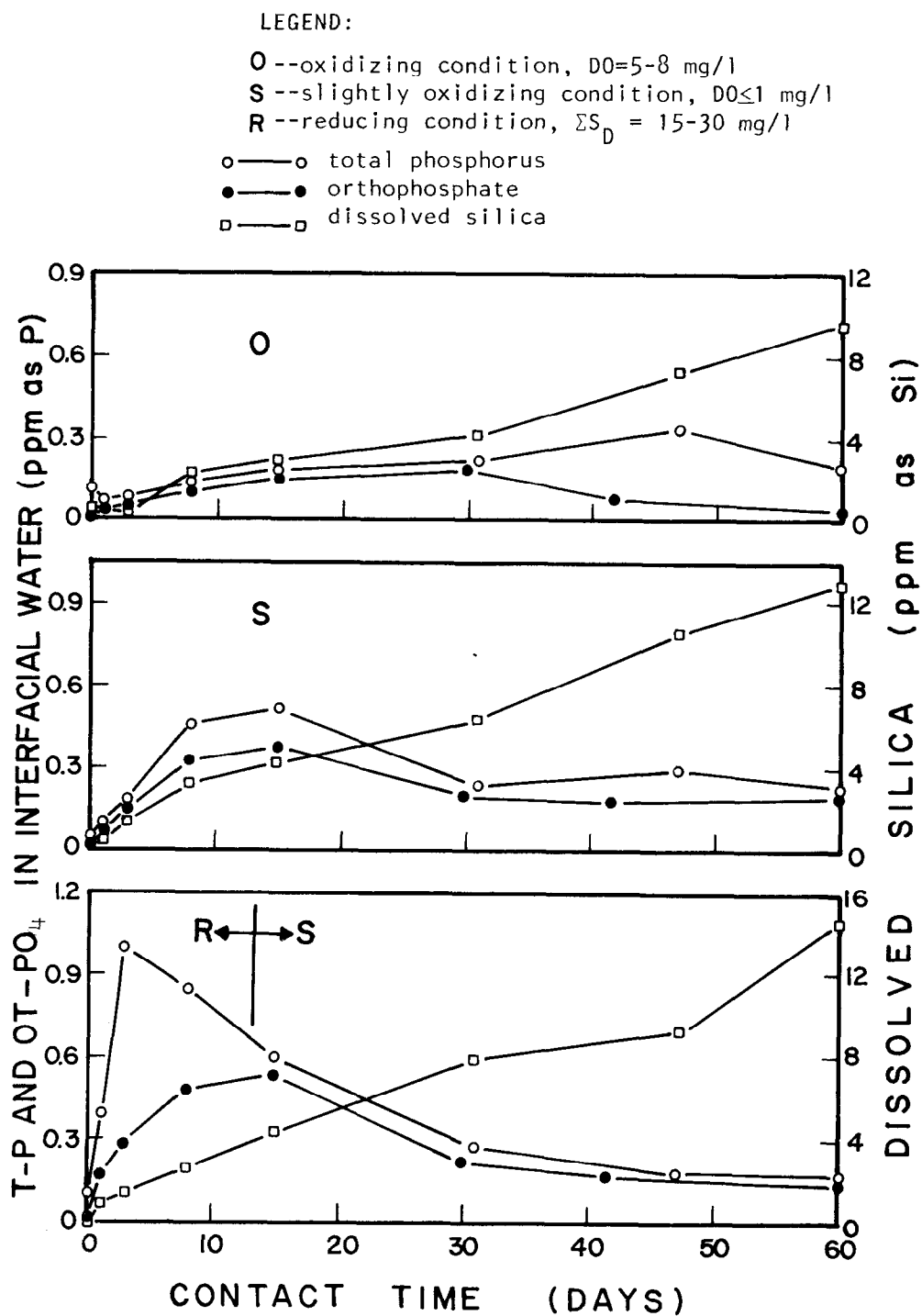
Figure 20. Transport of total phosphorus and orthophosphate
in sediment-seawater interfaces (sandy silt).
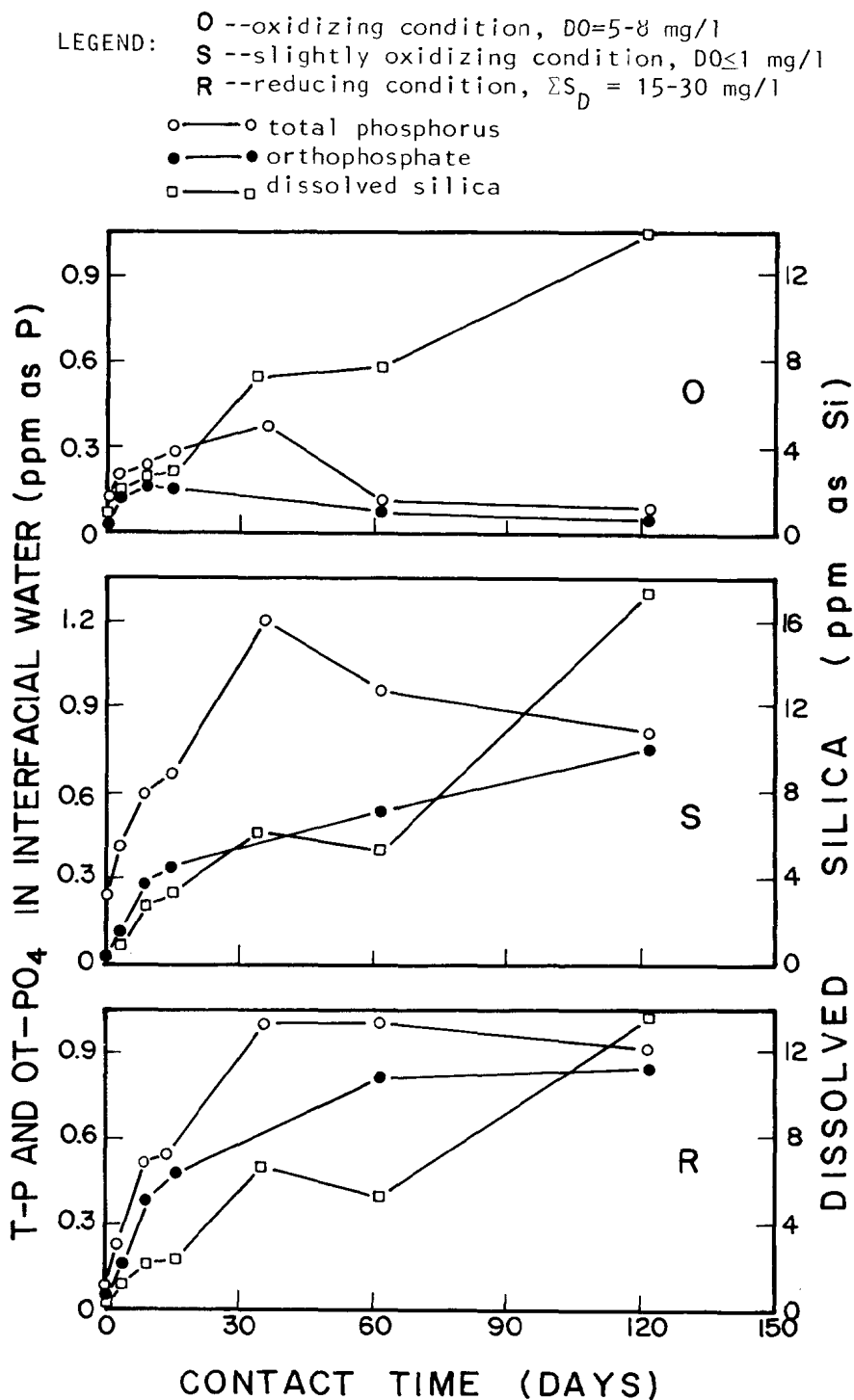
Figure 21. Transport of total phosphorus and orthophosphate in sediment-seawater interfaces (silty clay).
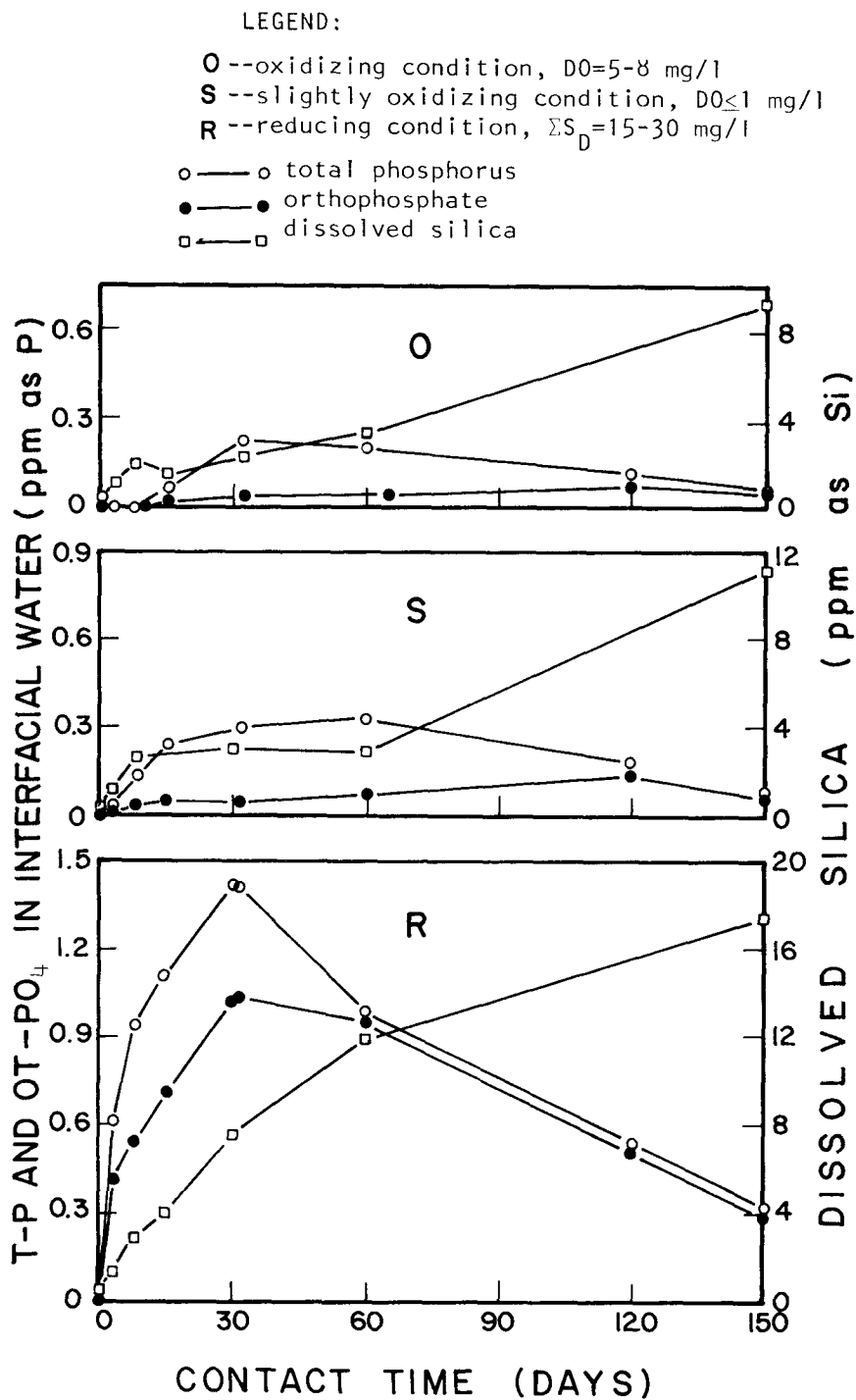
Figure 22. Transport of total phosphorus and orthophosphate in sediment-seawater interfaces (silty sand).
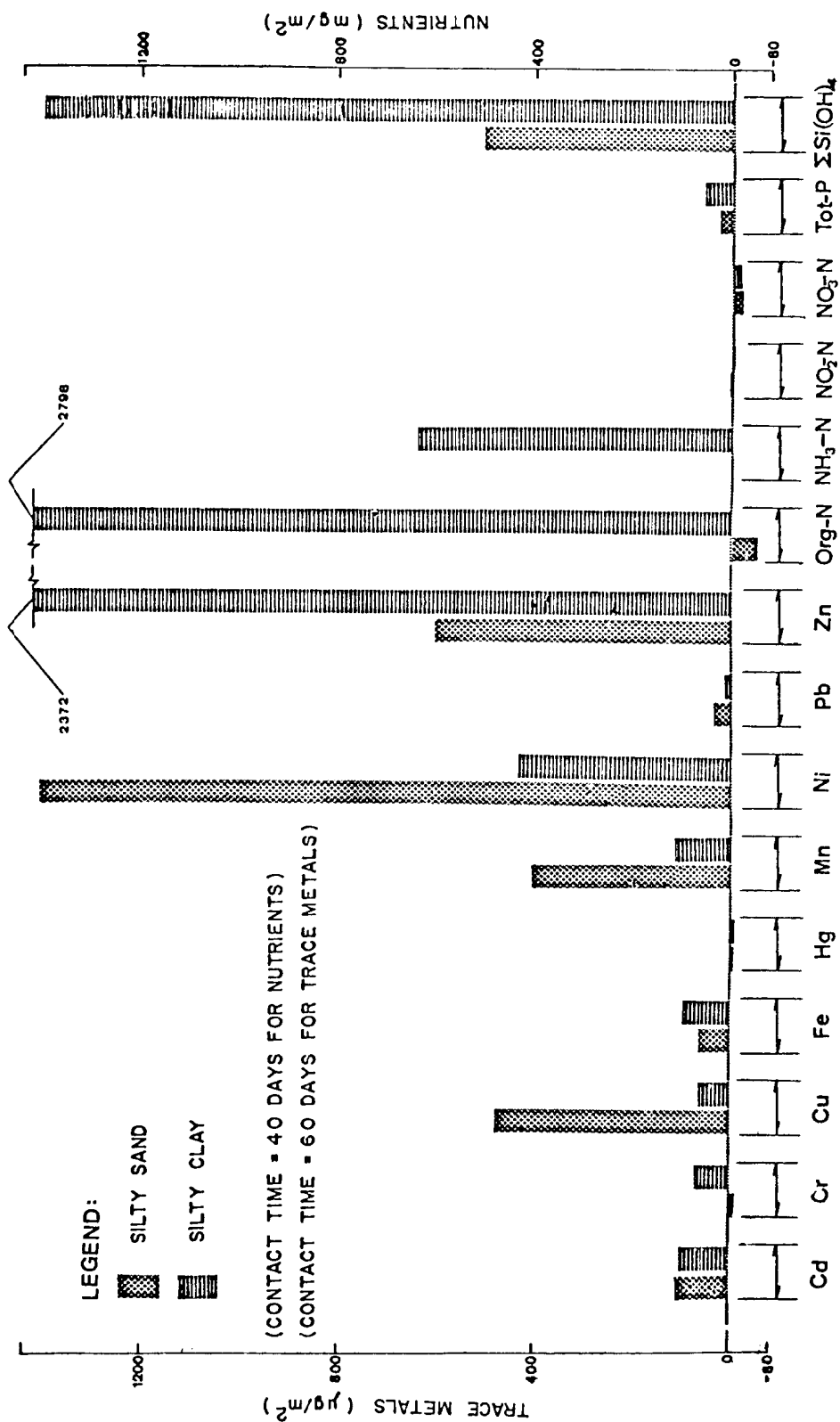
Figure 23. Transport of trace contaminants and nutrients from sediments (oxidizing condition).

201
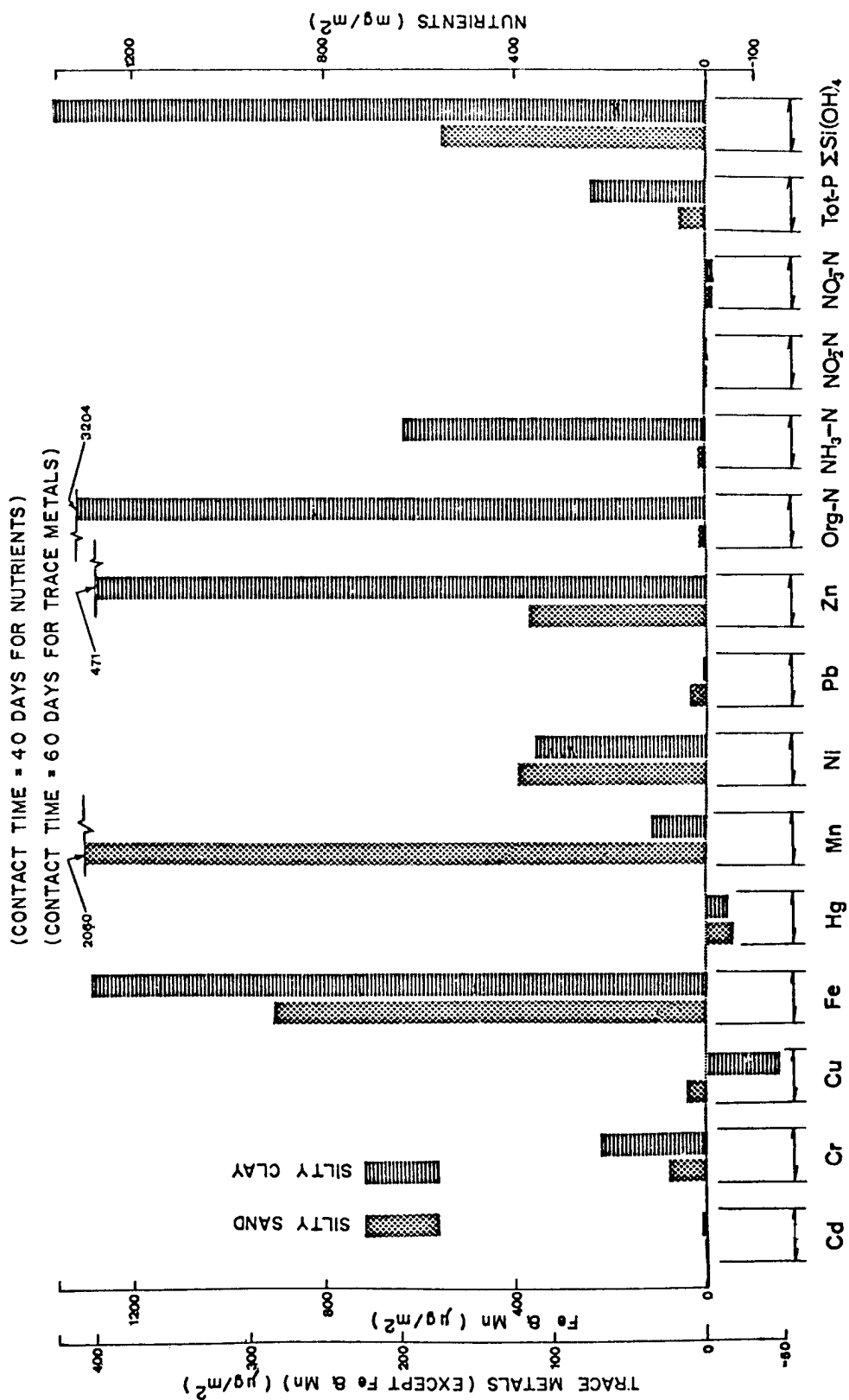
Figure 24. Transport of trace contaminants and nutrients from sediments (slightly oxidizing condition).

202
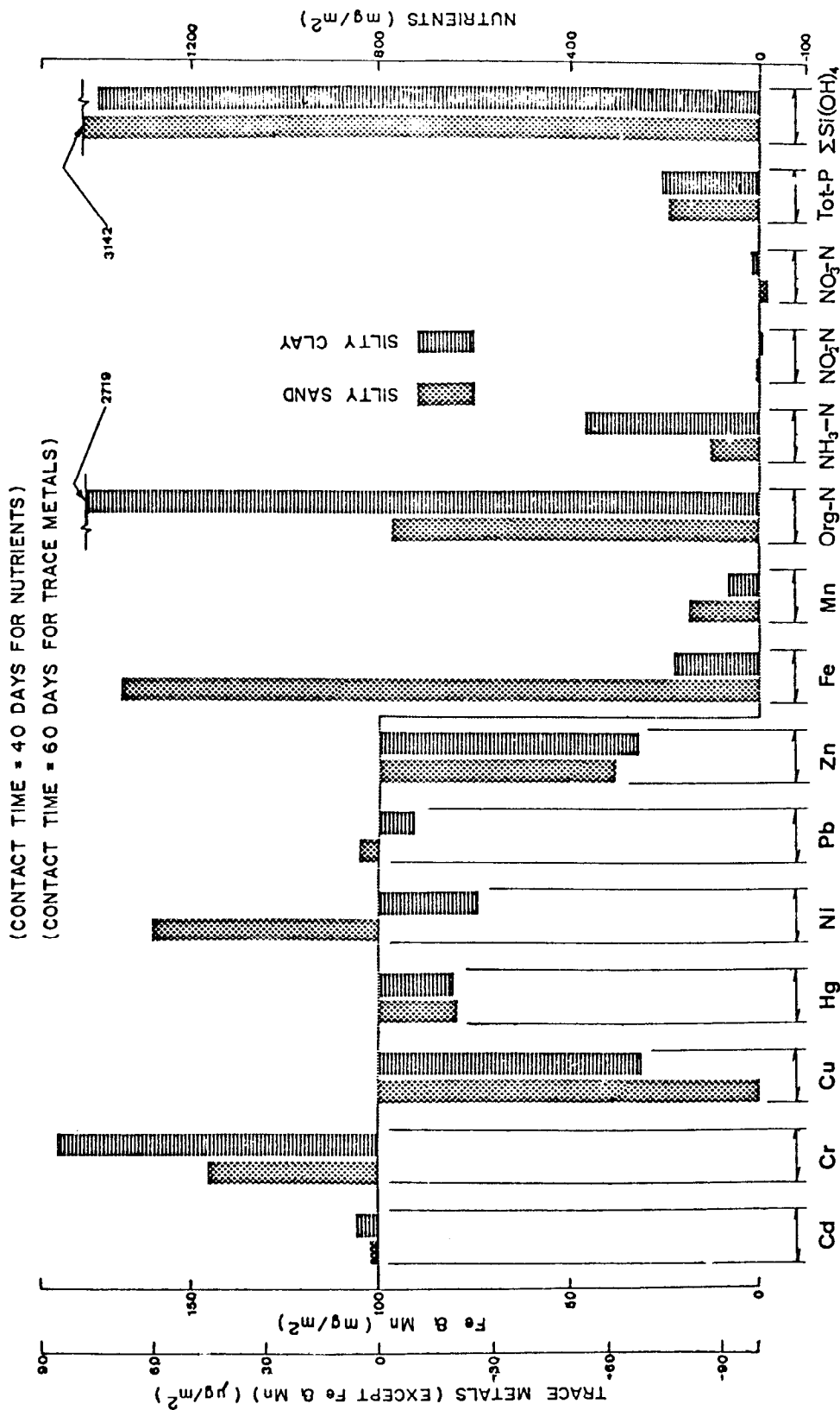
Figure 25. Transport of trace contaminants and
nutrients from sediments (reducing condition).
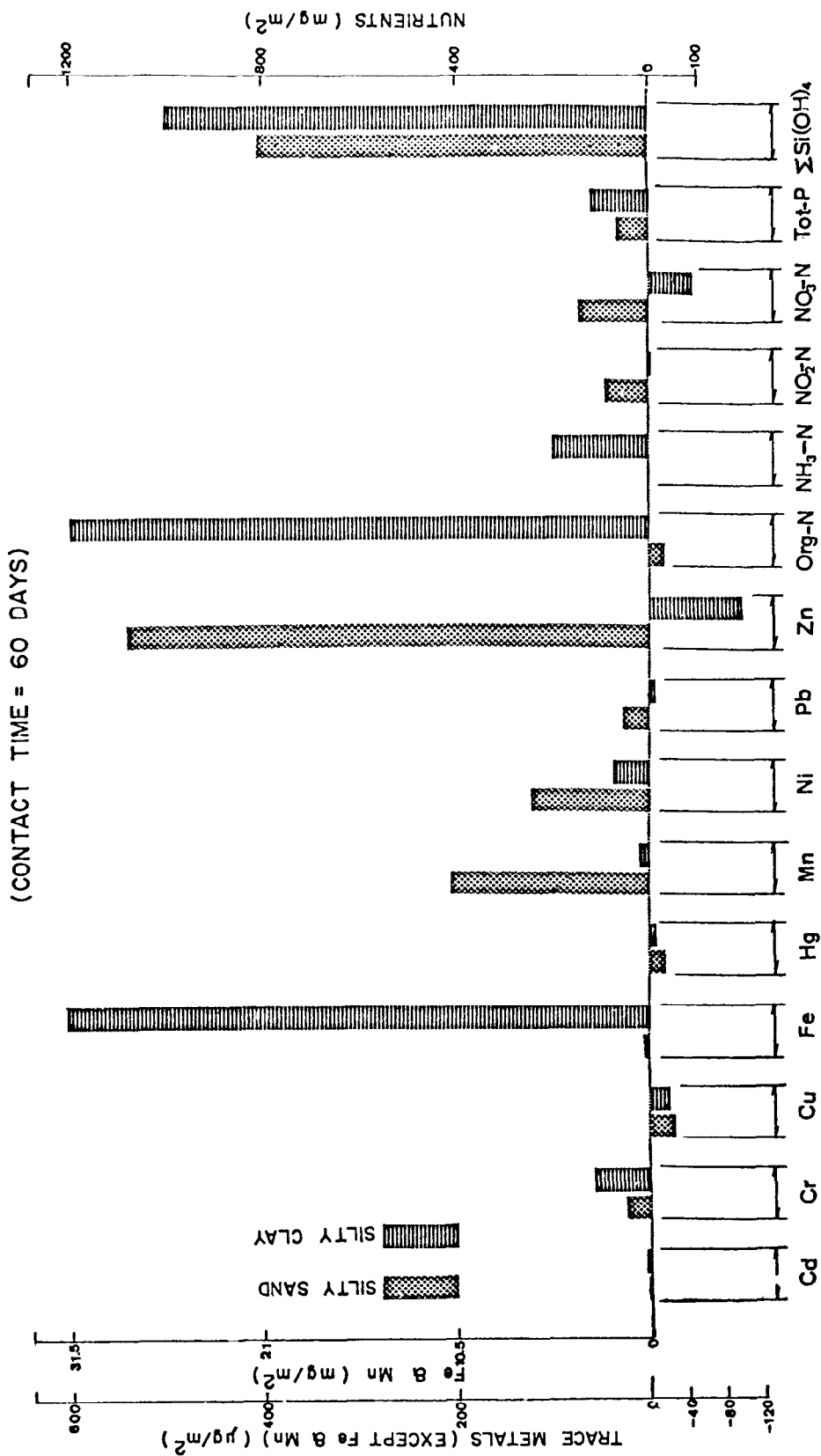
Figure 26. Transport of trace contaminants and
nutrients from sediments (resettled test).

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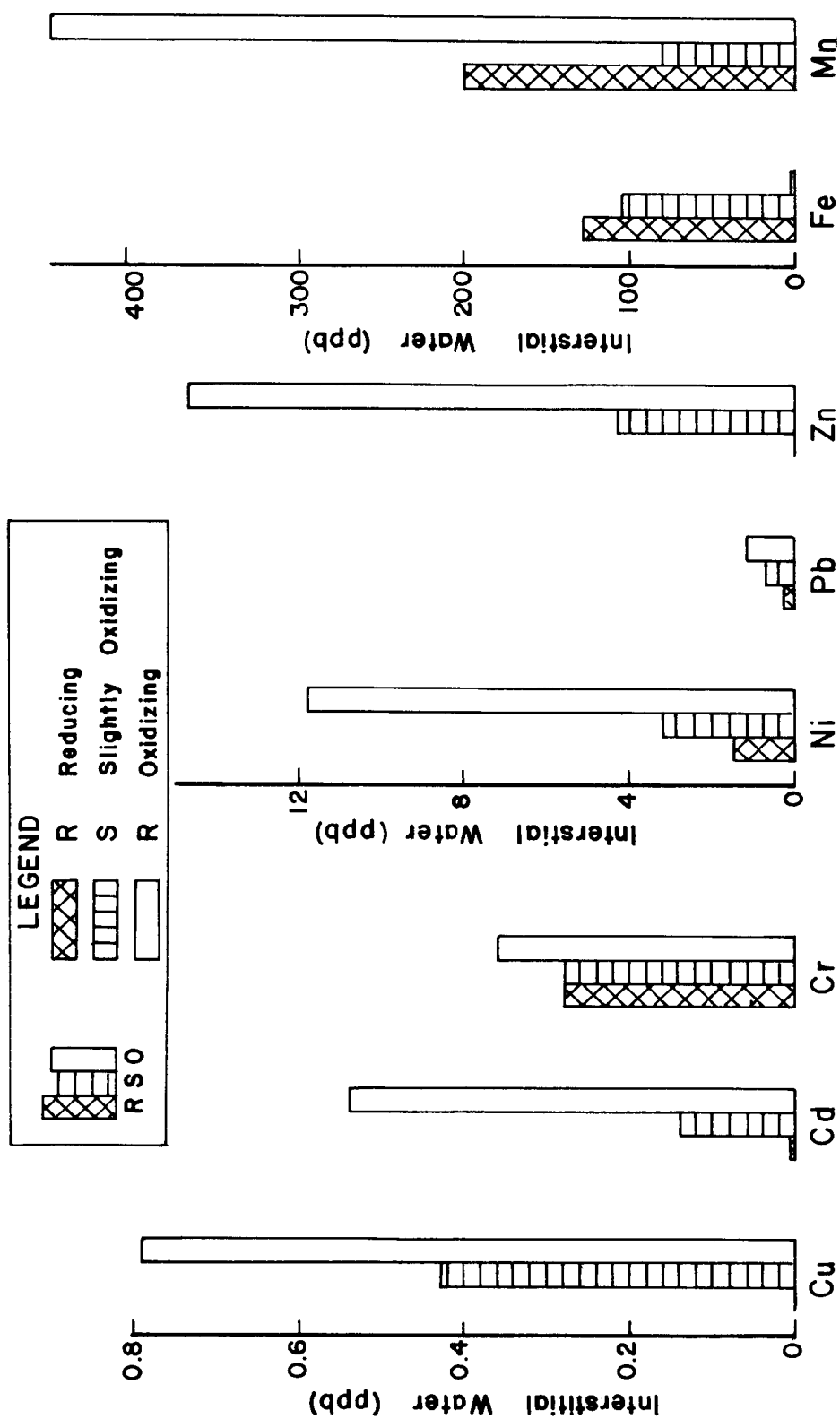
Figure 27. Concentration of trace metals in interstitial water after long-term incubation under different redox conditions (silty sand).
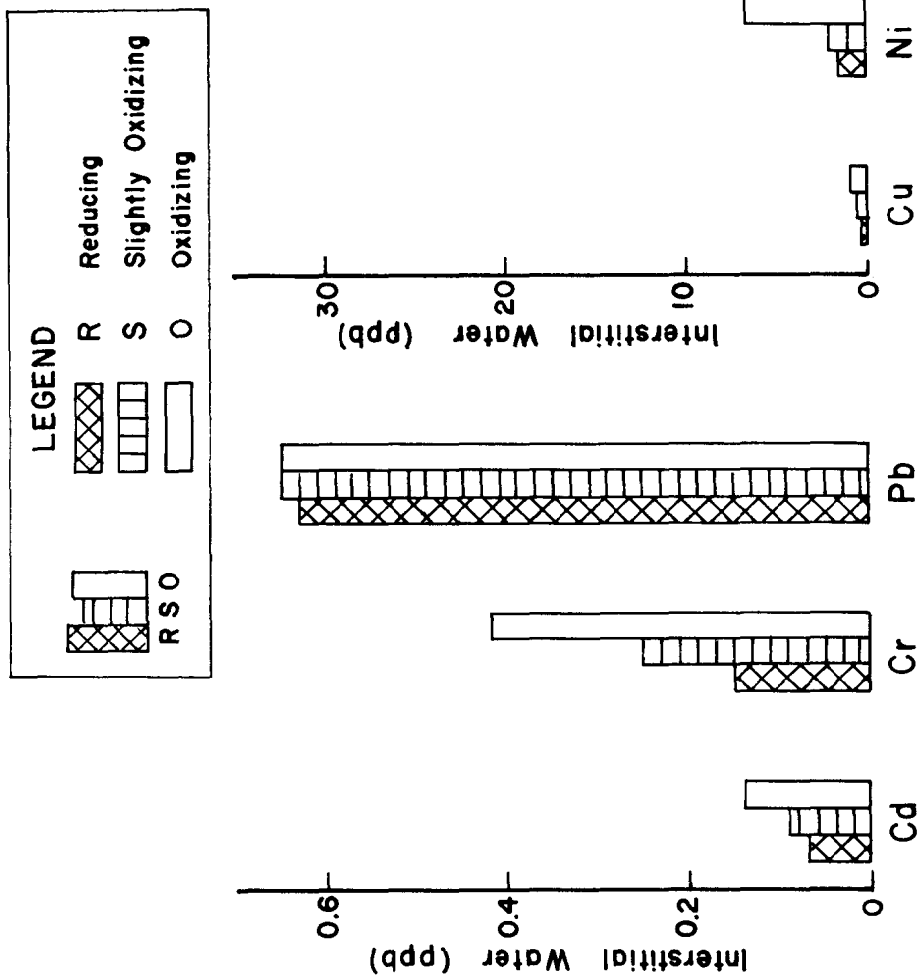
Figure 28. Concentration of trace metals in interstitial water after long-term incubation under different redox conditions (silty clay).
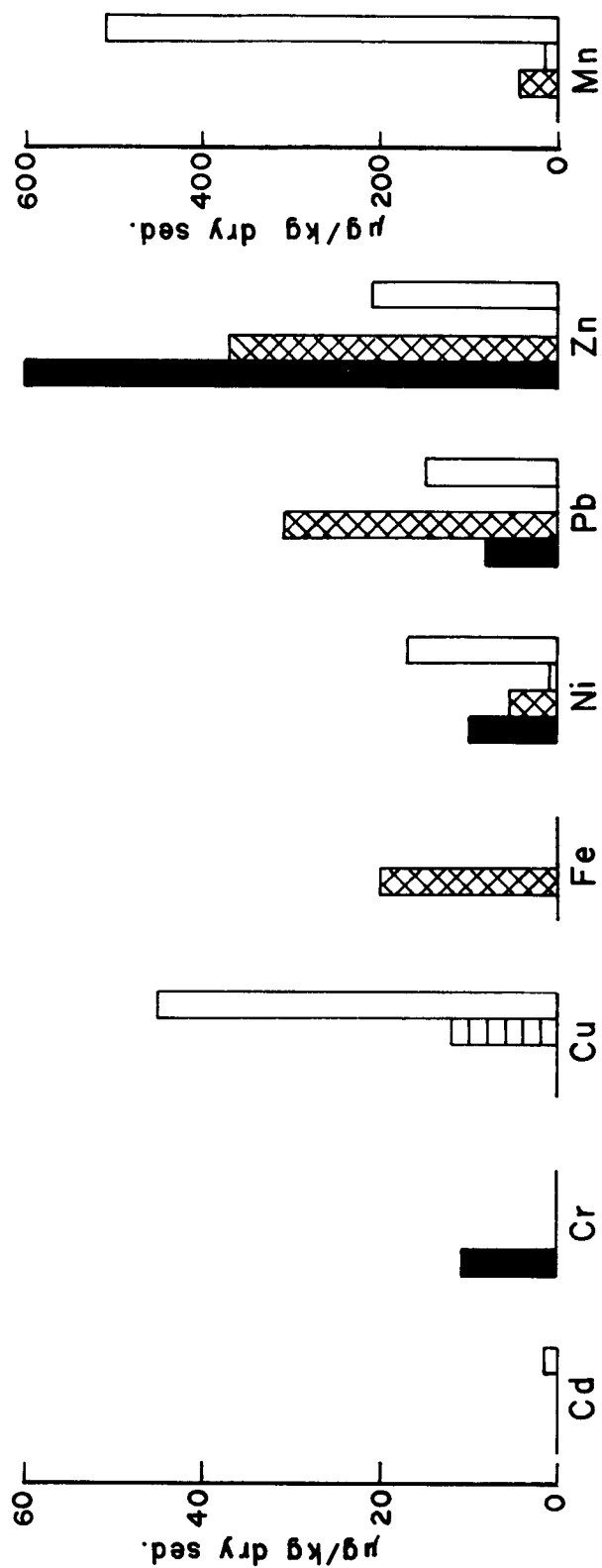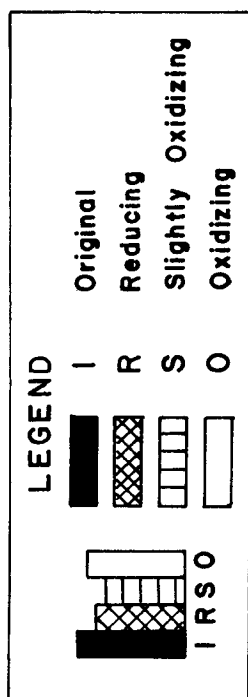
Figure 29. Concentration of trace metals in the water soluble phase after long-term incubation under different redox conditions (silty sand).
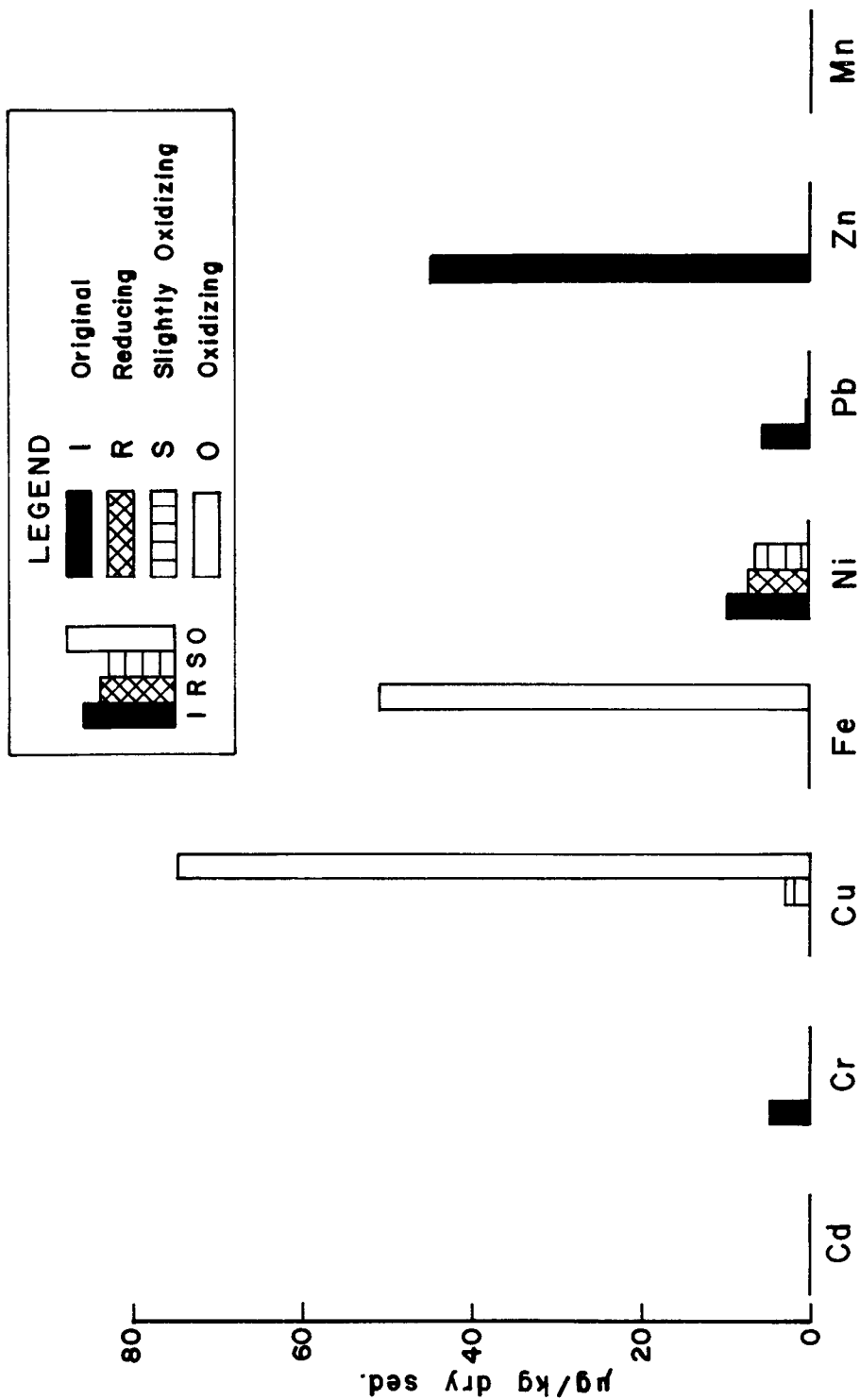
Figure 30. Concentration of trace metals in the water soluble phase after long-term incubation under different redox conditions (silty clay).
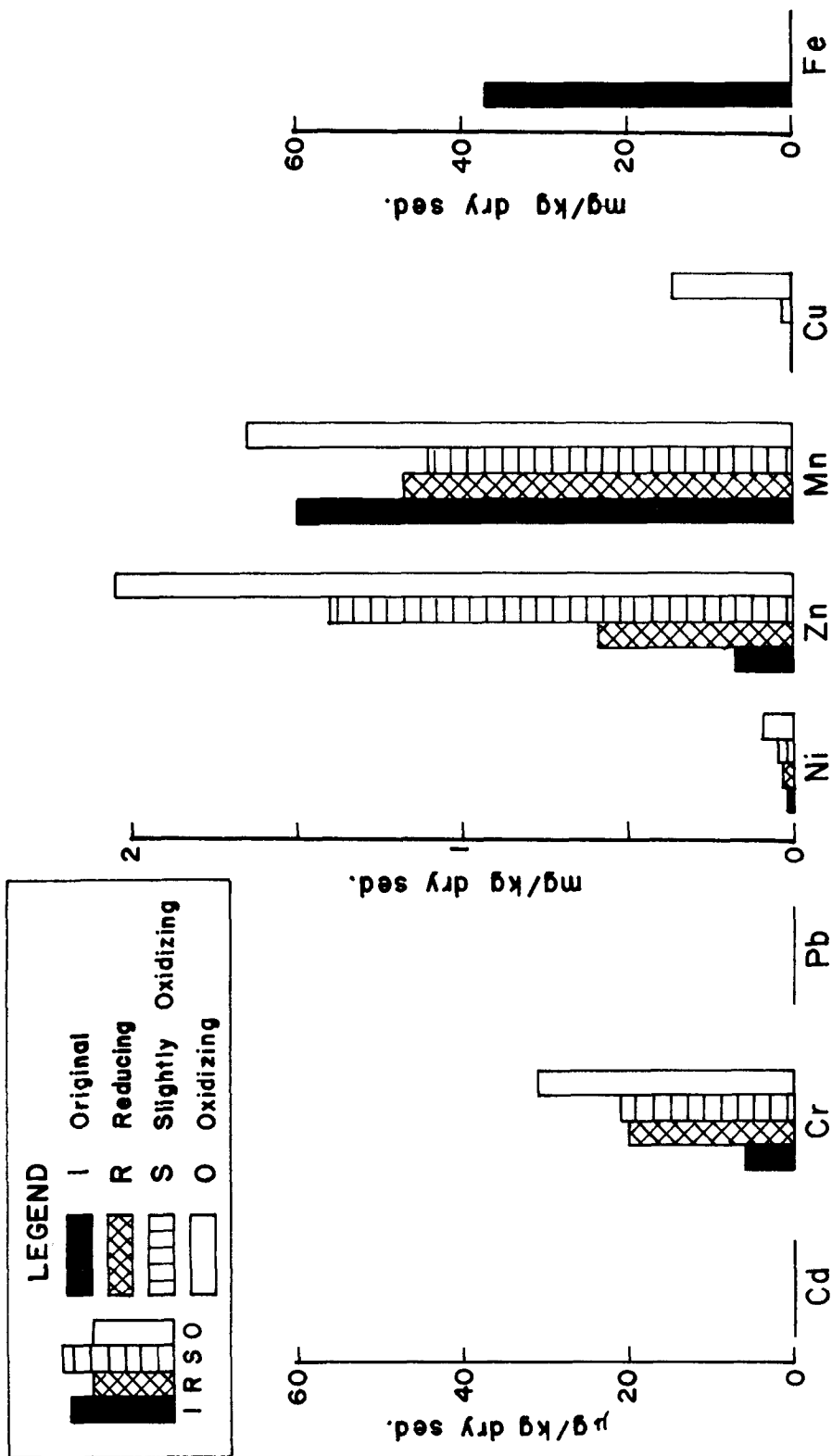
Figure 31. Concentration of trace metals in the exchangeable phase after long-term incubation under different redox conditions (silty sand).
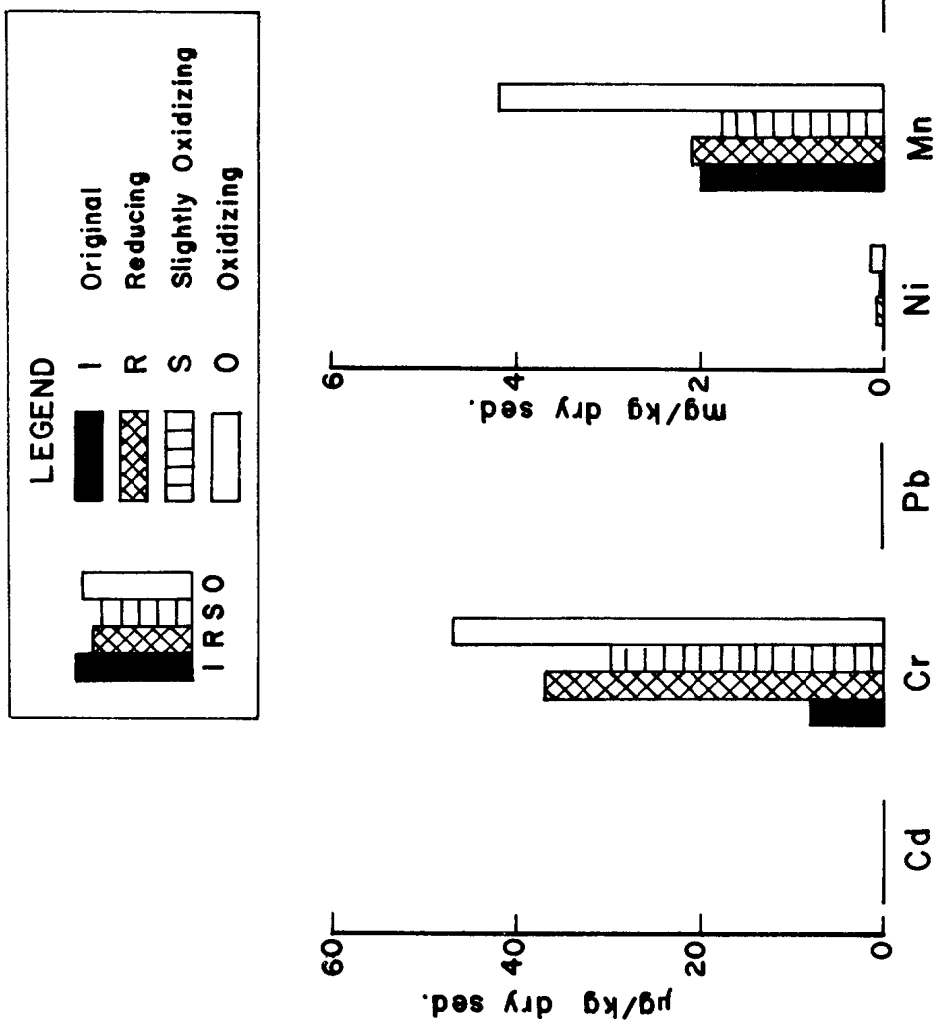
Figure 32. Concentration of trace metals in the exchangeable phase after long-term incubation under different redox conditions (silty clay).
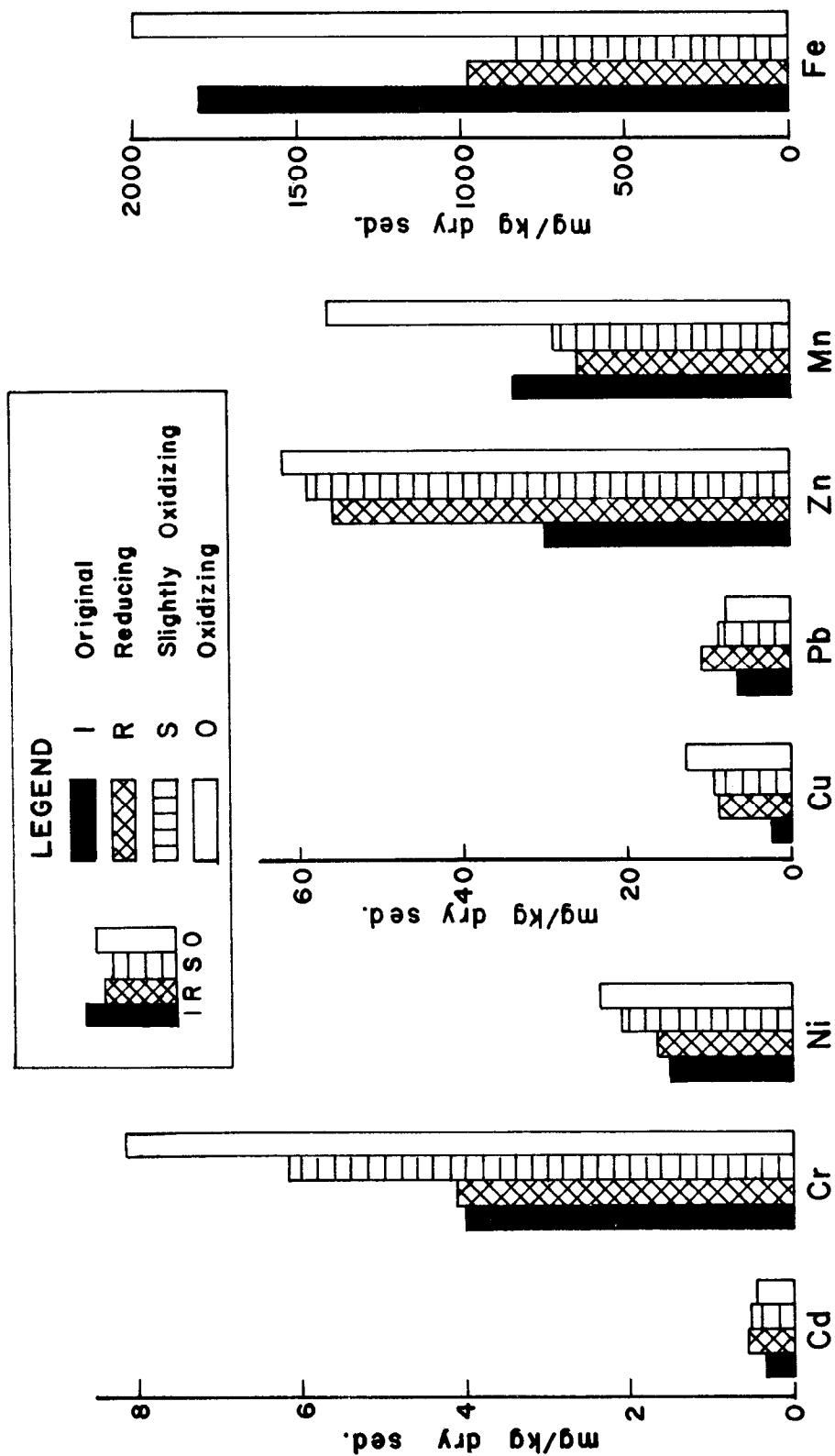
Figure 33. Concentration of trace metals in the acetic acid extractable phase after long-term incubation under different redox conditions (silty sand).

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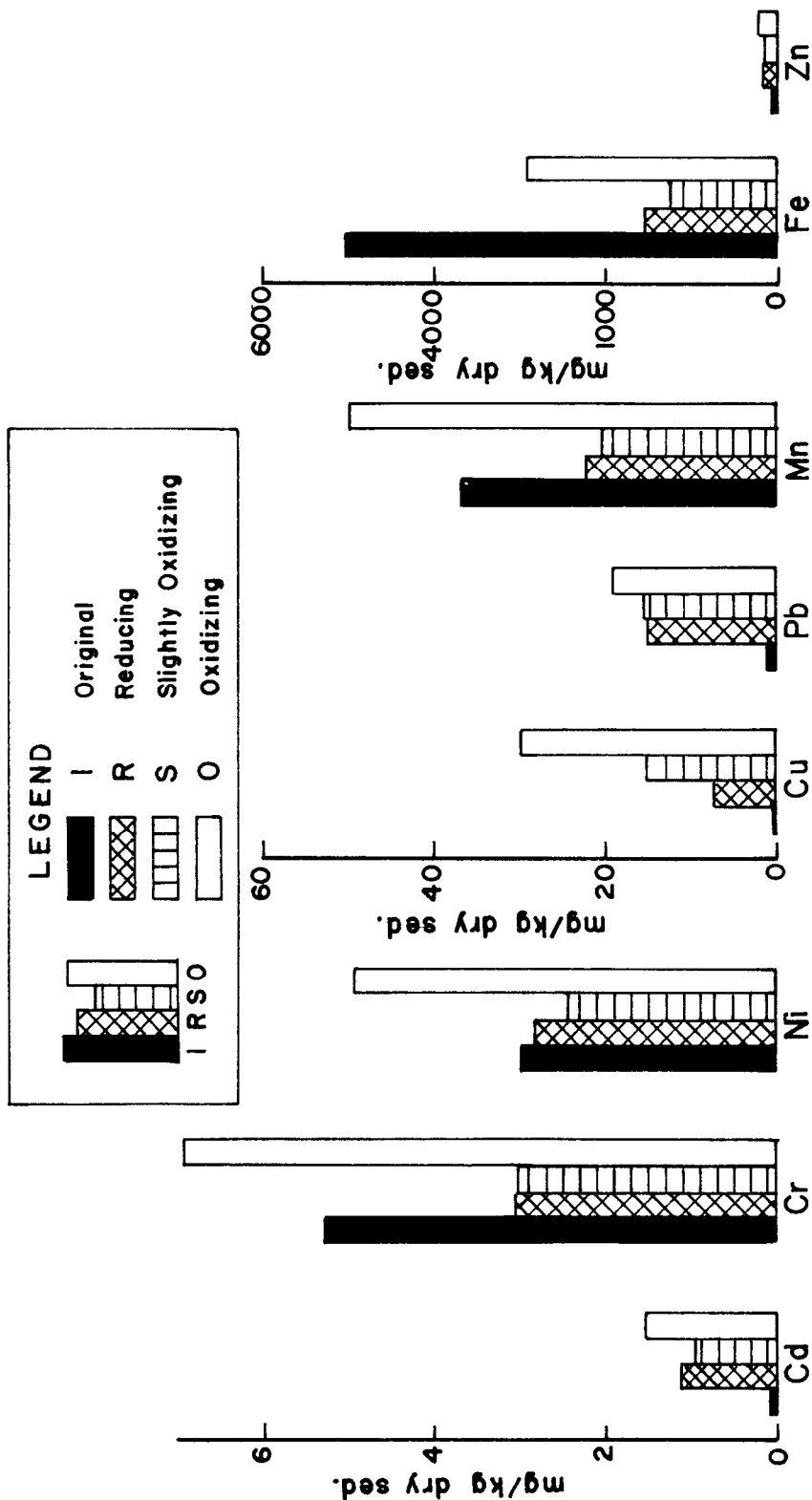
Figure 34. Concentration of trace metals in the acetic acid extractable phase after long-term incubation under different redox conditions (silty clay).

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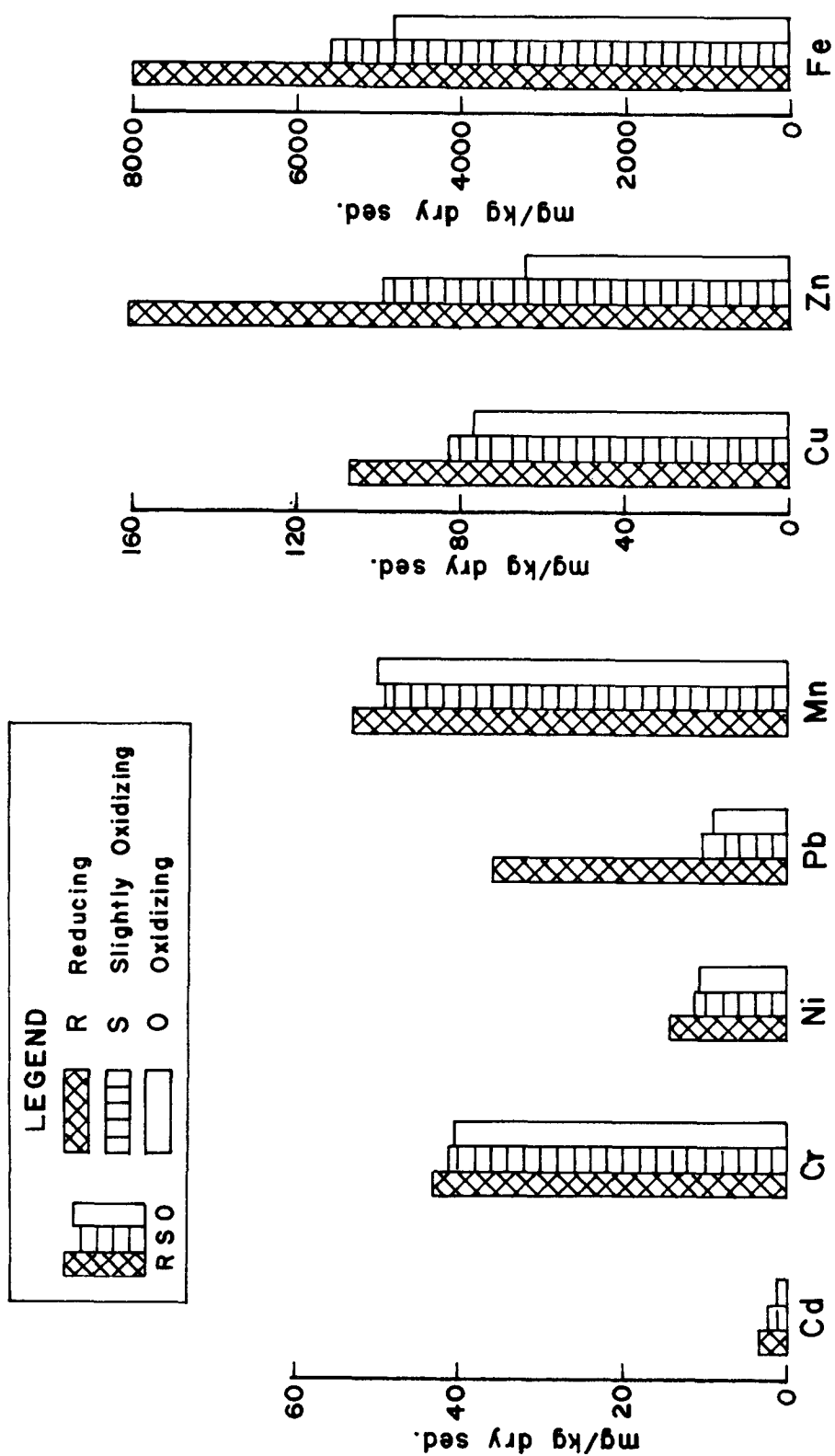
Figure 35. Concentration of trace metals in the organic-sulfide phase after long-term incubation under different redox conditions (silty sand).

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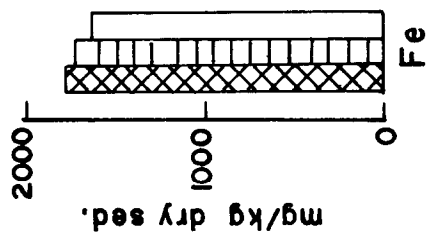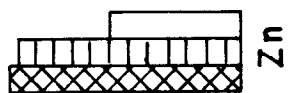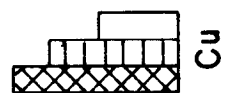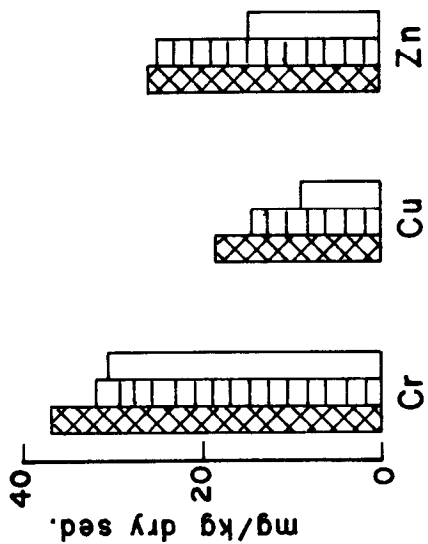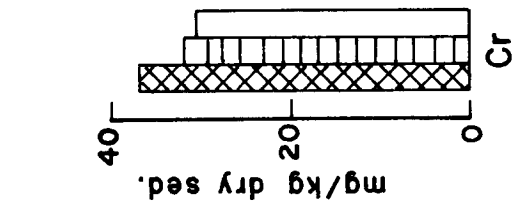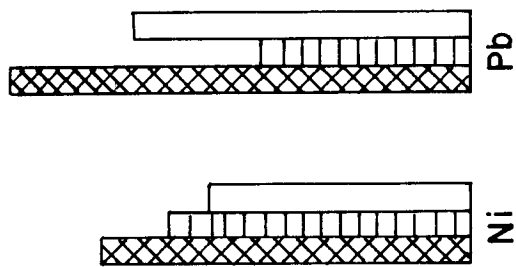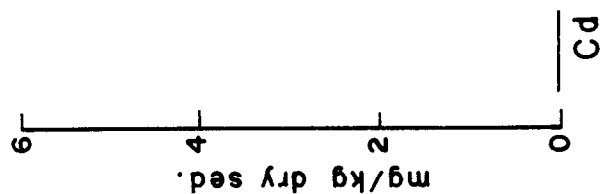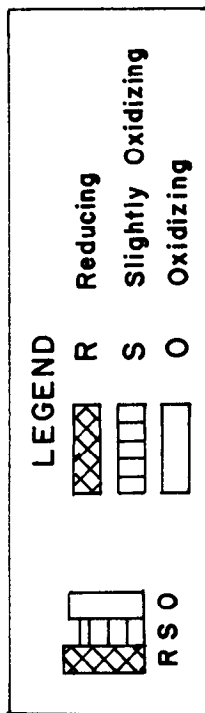
Figure 36. Concentration of trace metals in the organic-sulfide phase after long-term incubation under different redox conditions (silty clay).
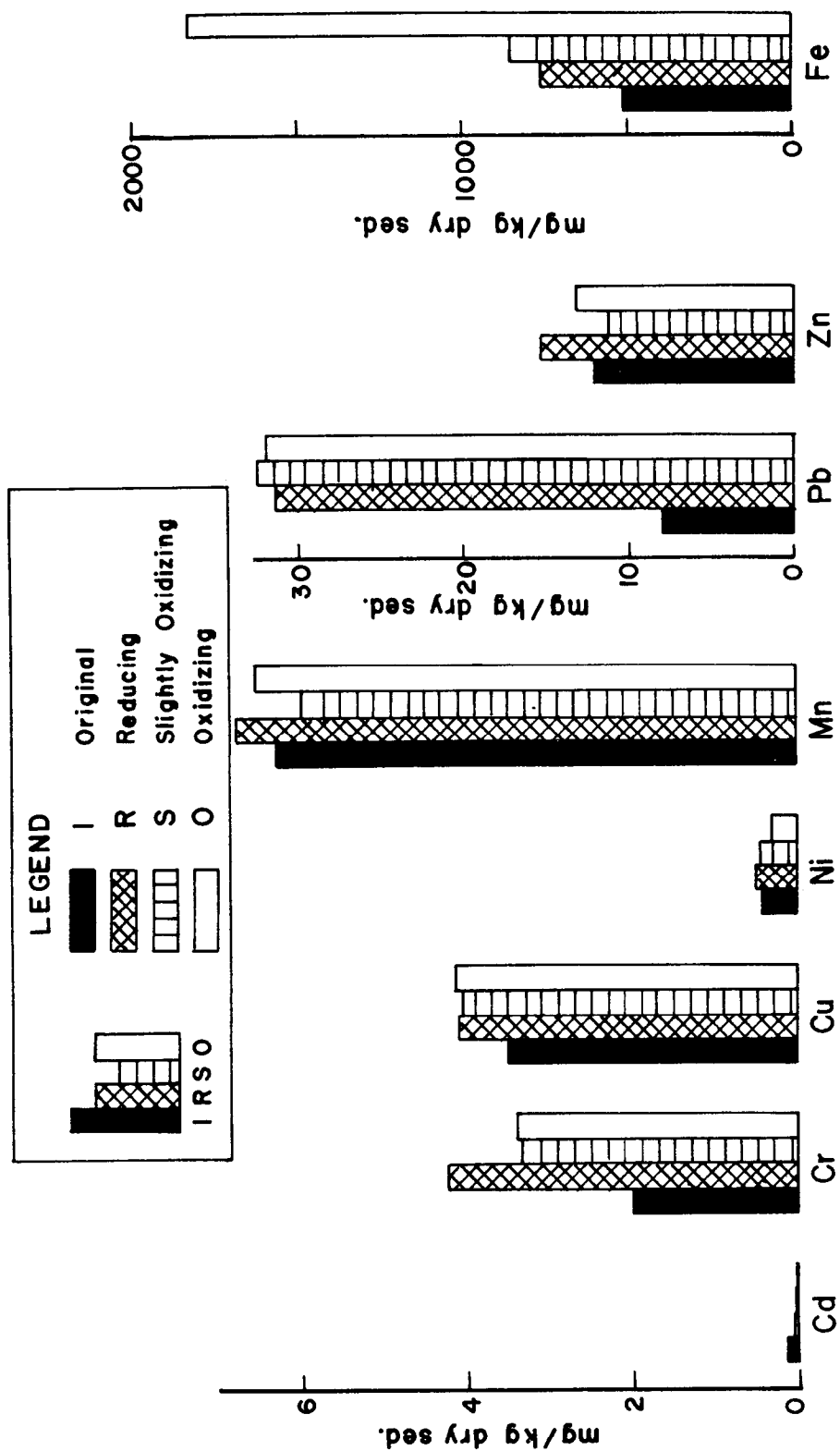
Figure 37. Concentration of trace metals in the easily reducible phase after long-term incubation under different redox conditions (silty sand).

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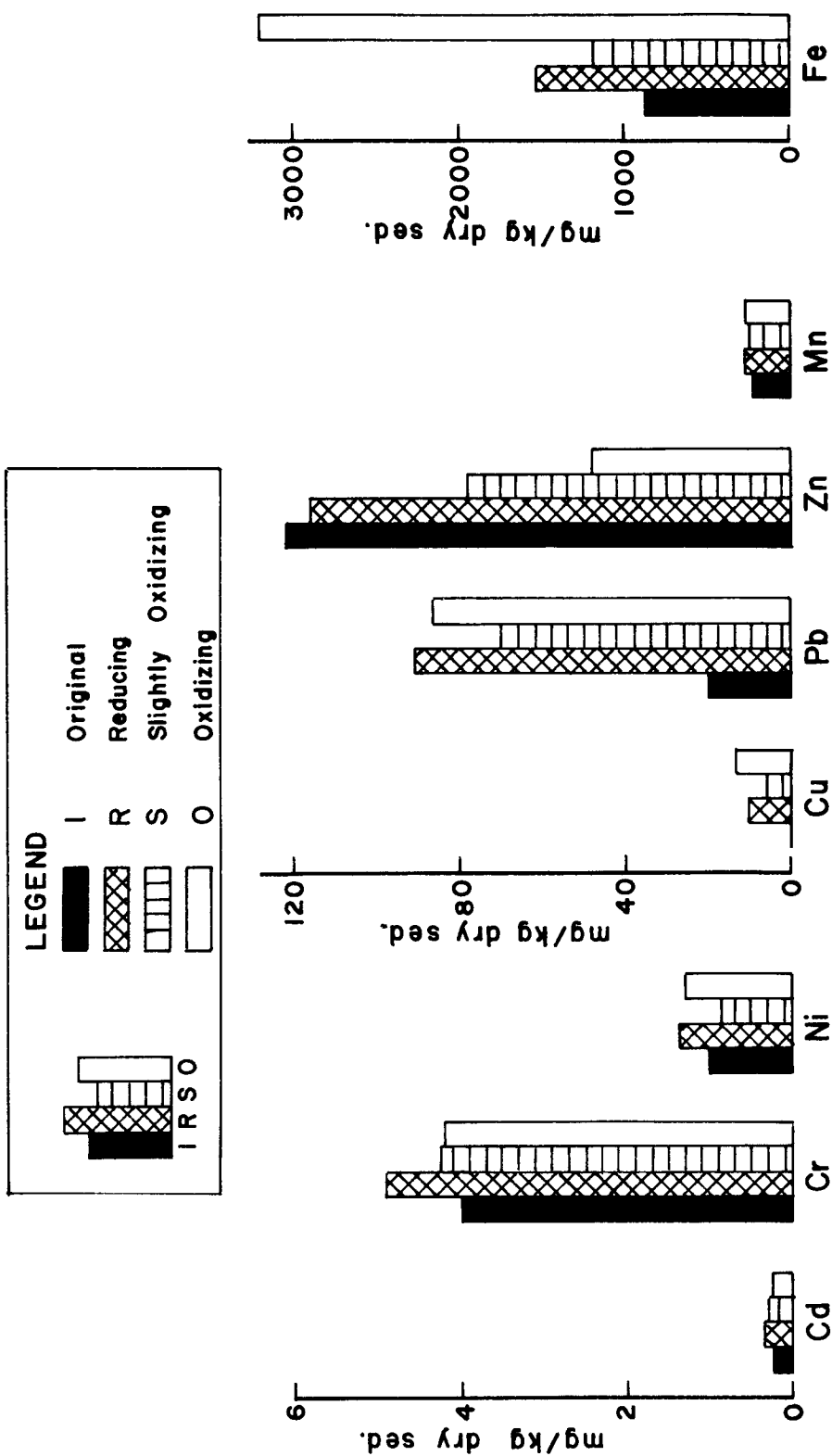
Figure 38. Concentration of trace metals in the easily reducible phase after long-term incubation under different redox conditions (silty clay).

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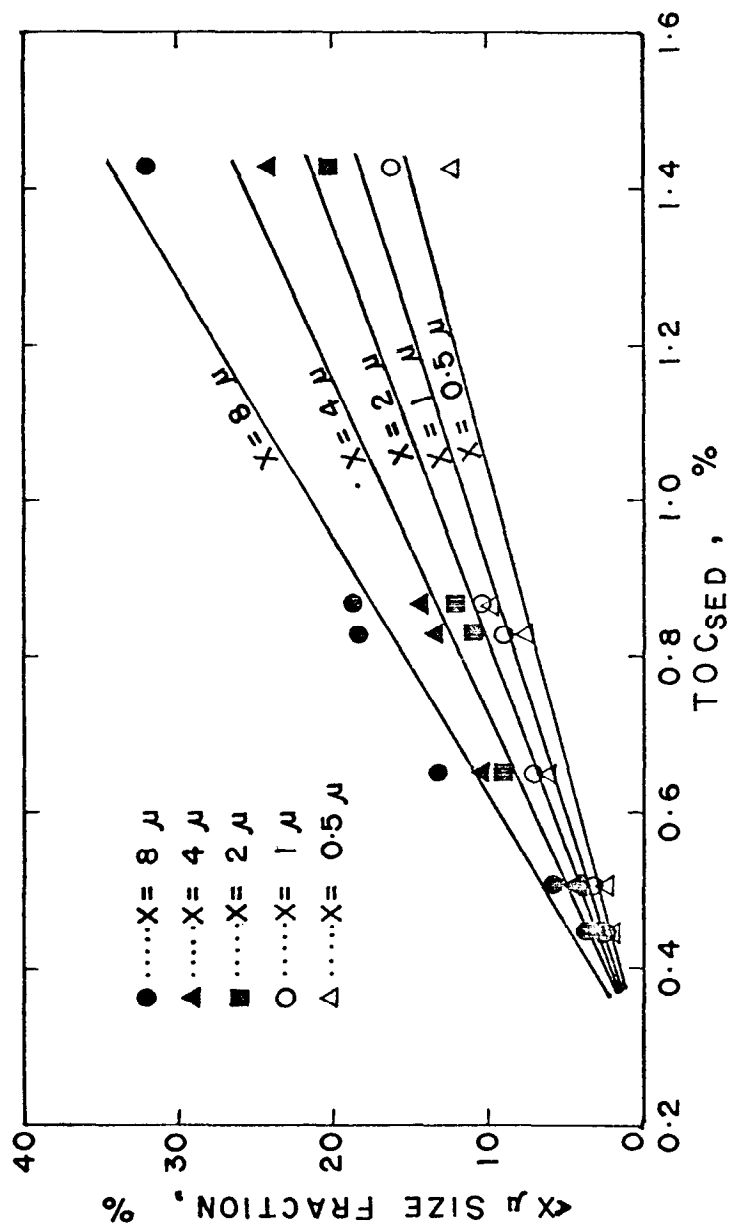
Figure 39. Relationship of particle size and total organic carbon in the sediments.
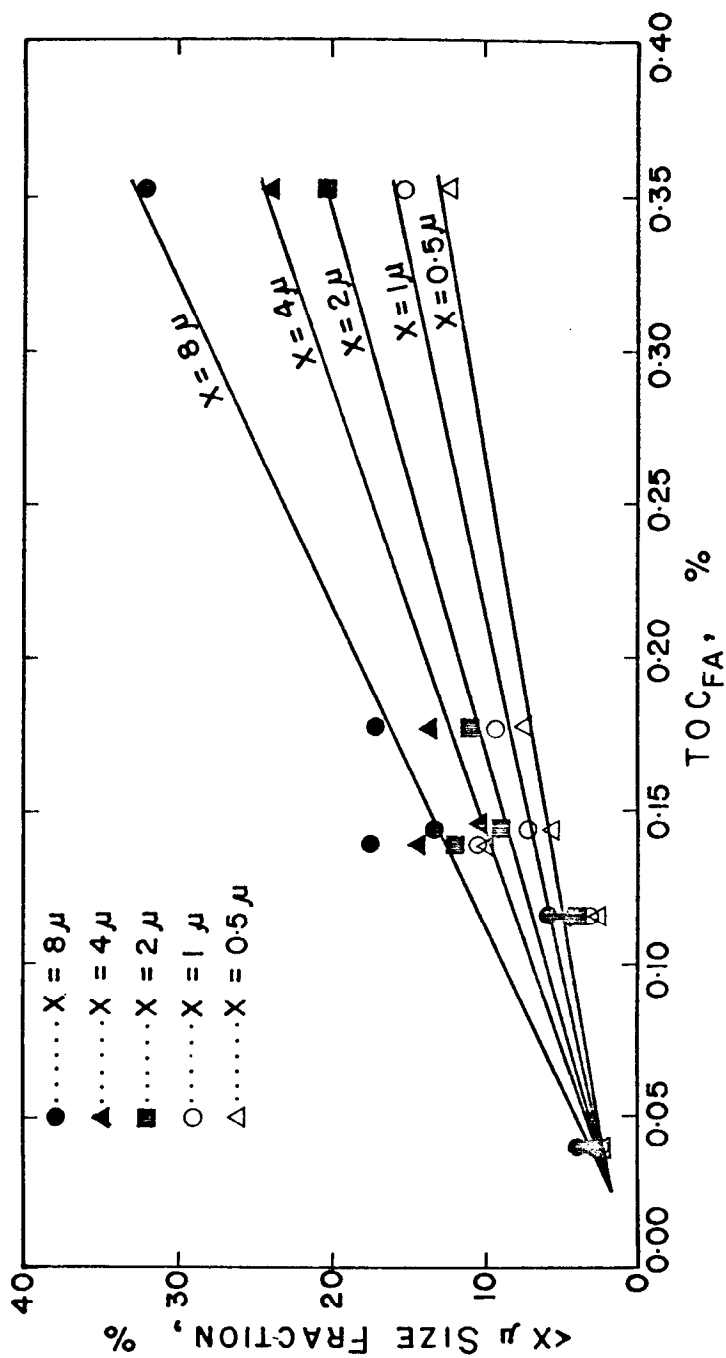
Figure 40. Relationship of the particle size and total organic carbon of the fulvic acid fraction in the marine sediments.
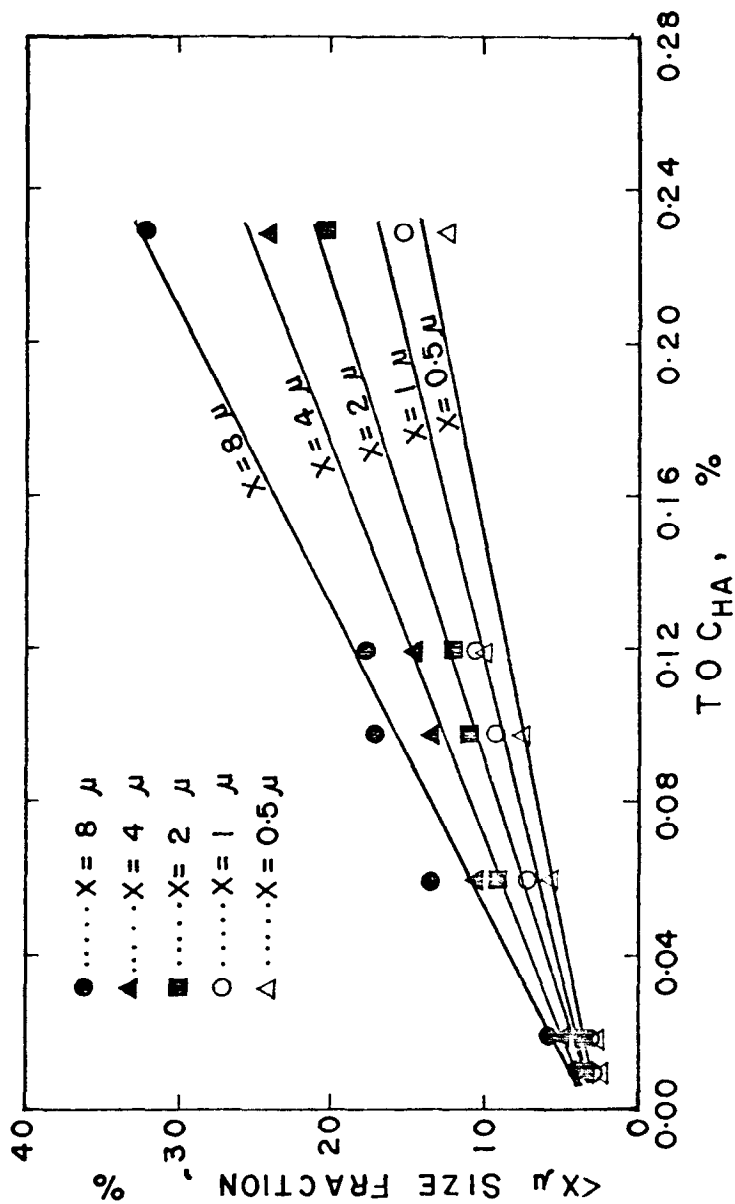
Figure 41. Relationship of the particle size and total organic carbon of the humic acid fraction in the marine sediments.

Figure 42. Relationship of total organic carbon and total DDT in the marine sediments.

Figure 43. Relationship of total organic carbon and total chlorinated hydrocarbons in the marine sediments.